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NEIGHBORHOOD SCALE AIR QUALITY MODELING IN CORPUS CHRISTI USING AERMOD AND CALPUFF

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BY

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Ambient monitoring and air quality modeling of air toxics concentrations at the neighborhood-scale level is a key element for human exposure and health risk assessments. Since 2005, The University of Texas at Austin (UT) has operated a dense ambient monitoring network that includes both hourly automated gas chromatographs as well as threshold triggered canister samples and meteorological data in the Corpus Christi area. Although Corpus Christi is in attainment with the National Ambient Air Quality Standards for both ozone and fine particulate matter, its significant petroleum refining complex has resulted in concerns about exposure to air toxics. The seven site network, incorporating both the industrial and residential areas in Corpus Christi, provided a unique opportunity to further the development and understanding of air quality modeling for toxic air pollutants at the neighborhood-scale level. Two air dispersion models, AERMOD and CALPUFF, were used to predict air concentrations of benzene for one of the UT operated monitoring sites (Oak Park monitoring site: C634) and the predictions were compared to the observed benzene concentration data at the Oak Park monitoring site to evaluate model performance. AERMOD and CALPUFF were also used to predict

benzene concentrations in populated areas and at sensitive receptor locations such as schools and hospitals.

Both AERMOD and CALPUFF were able to reproduce the early morning high benzene concentration and the northern wind effect except under strong NNE wind conditions, where the observed data indicated elevated high benzene concentration which AERMOD and CALPUFF failed to predict. These under-predictions could be due to the NNE strong wind condition at that time of these occurrences or could be attributed to different types of emissions other than the point sources emissions from the 2005 TCEQ Photochemical Modeling inventory, such as mobile sources or accidental emission events. These preliminary analyses could be expanded by modeling longer periods, by including other emission sources and by inter-comparisons with observed data from other CCNAT monitoring sites. In addition, fundamentally different modeling approaches (eulerian, rather than lagrangian) could be considered.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1 INTRODUCTION

Background

Urbanization and industrialization have important consequences for the atmosphere. Increasing energy consumption and production can be followed by emissions of pollutants that affect human health and welfare (Molina et al., 2004). The U.S. Environmental Protection Agency (EPA) has established National Ambient Air Quality Standards (NAAQS) for six criteria pollutants in order to protect human health and public welfare: carbon monoxide (CO), sulfur dioxide (SO_2), lead (Pb), nitrogen dioxide (NO_2), ozone (O_3), and particulate matter (PM). In addition, toxic air pollutants, also known as hazardous air pollutants (HAPs) or air toxics are pollutants that are classified by the U.S. Environmental Protection Agency (EPA) as known or suspected human carcinogens or as having other adverse environmental or human health impacts, including reproductive, developmental, neurological, and respiratory effects (Rosenbaum et al., 1999; http://www.epa.gov/airtoxics/brochure.html). Section 112 of the Clean Air Amendments of 1990 identified 189 toxic air pollutants, which were subject to regulatory control. Examples of HAPs include compounds such as benzene, acrolein, ethylbenzene, acetalydehyde, 1,3-butadiene, dioxin, asbestos, and metals such as cadmium, mercury, and lead compounds (List of Hazardous Air Pollutants; http://www.epa.gov/ttn/atw/orig189.html).

Air pollutants can be emitted directly from a source (primary pollutants) or formed in the atmosphere by physical and chemical processes (secondary pollutants). Ozone is an example of a secondary pollutant as it is formed by photochemical reaction of nitrogen oxides (NO_x) and VOCs (Sillman et al, 1999). Historically, most urban

emissions measurements have been focused on pollutants or pollutant precursors involved in photochemical oxidant production (e.g. ozone) and/or primary or secondary aerosol particle loadings (Mobley et al, 2004). But recently, there is growing interest in the emission sources and ambient concentration levels of air toxics, species that are known or suspected to directly impact human health without photochemical processing. EPA has identified four emission source categories for air toxics and other air pollutants: stationary point, mobile, biogenic, and area (Air Pollution Emissions Overview; http://www.epa.gov/air/oaqps/emissns.html). Point sources include large stationary commercial or industrial facilities such as manufacturing facilities and electric power plants; mobile sources include on-road vehicles such as light-duty gasoline passenger vehicles and trucks, light-duty and heavy-duty diesel vehicles and motorcycles that operate on public highways and roadways, as well as non-road sources operating off public roadways such as aircrafts, recreational boats, lawn and garden equipment, and small engines used in industrial and construction operations. Biogenic emissions originate from natural sources such as bacteria, plants and trees. Area sources are stationary point sources that are too small or numerous to be characterized individually, such as gasoline service stations, small paint shops, and consumer use of solvents. Emission from these sources are typically estimated collectively and spatially allocated according to surrogates such a population or income.

Emissions of air toxics are tracked on a national-scale through the Toxics Release Inventory (TRI) Program, which compiles annual reported emissions from industrial point sources that meet threshold emissions levels, and the National Emission Inventory for HAPs, which compiles emissions from different anthropogenic source sectors across the US on a three-year cycle, and through state or local-scale efforts (National Emission Inventory Database; http://www.epa.gov/oar/data/neidb.html). The National Air Toxics

Assessment (NATA) is conducted by the EPA to identify air toxics, emission source types, and locations which are of greatest potential concern in terms of contributing to chronic cancer and non-cancer health risks (National Air Toxics Assessments; http://www.epa.gov/ttn/atw/natamain/). Three NATAs have been conducted to date, for 1996 and 1999, and most recently for 2002, the results of which were released in June 2009 (http://www.epa.gov/ttn/atw/nata2002/). The NATA process is comprised of four elements: (1) compilation of a national emissions inventory of air toxics emissions from outdoor sources; (2) estimation of ambient concentrations of air toxics across the US using dispersion models; (3) estimation of population exposures across the US; and (4) characterization of the potential public health risk due to inhalation of air toxics including both cancer and non-cancer effects (National Air Toxics Assessments; http://www.epa.gov/ttn/atw/natamain/). The results of the most recent NATA indicated that local industrial emissions (having local or hotspot effects) account for approximately 25 percent of the average overall cancer risk and mobile sources account for approximately 30 percent (NATA 2002 Fact sheet; http://www.epa.gov/ttn/atw/nata2002/factsheet.html). The NATA is not intended to provide comprehensive risk assessments for local areas or "hotspots" or for regulatory action, but rather to prioritize substances, sources, and regions for further study and potential community efforts (National Air Toxics Assessments; http://www.epa.gov/ttn/atw/natamain/).

The University of Texas at Austin (UT) has on-going projects to conduct ambient monitoring and neighborhood-scale air quality modeling of air toxics concentrations in the Corpus Christi area. Although Corpus Christi is in attainment with the National Ambient Air Quality Standards for both ozone and fine particulate matter, its numerous refineries and chemical industries are sources of air toxics. The close proximity of the

Corpus Christi industrial complex to residential neighborhoods has raised concerns about human exposure to air toxics. Figure 1.1 shows the major location of Corpus Christi industrial facilities along the ship channel and the population density of the region is shown in Figure 1.2.

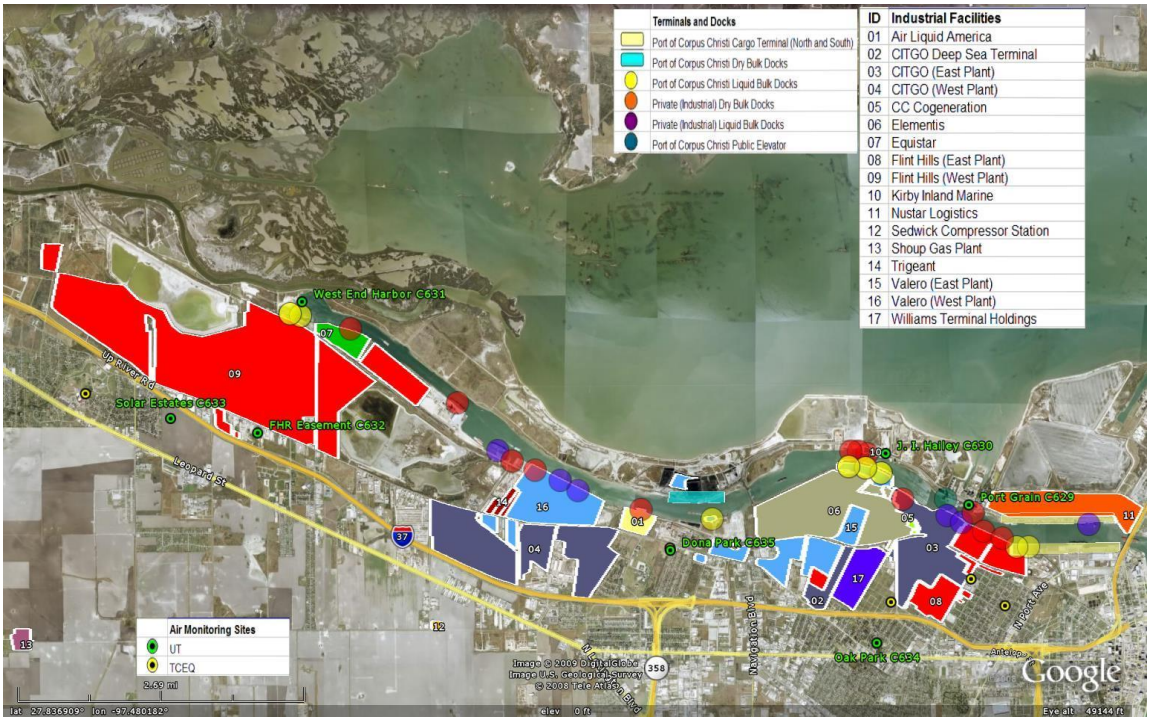

Figure 1.1 Locations of industrial facilities that are characterized by non-zero VOC emissions in the 2005 TCEQ Photochemical Modeling EI
(Source: Gary McGaughey, et. al, 2009)

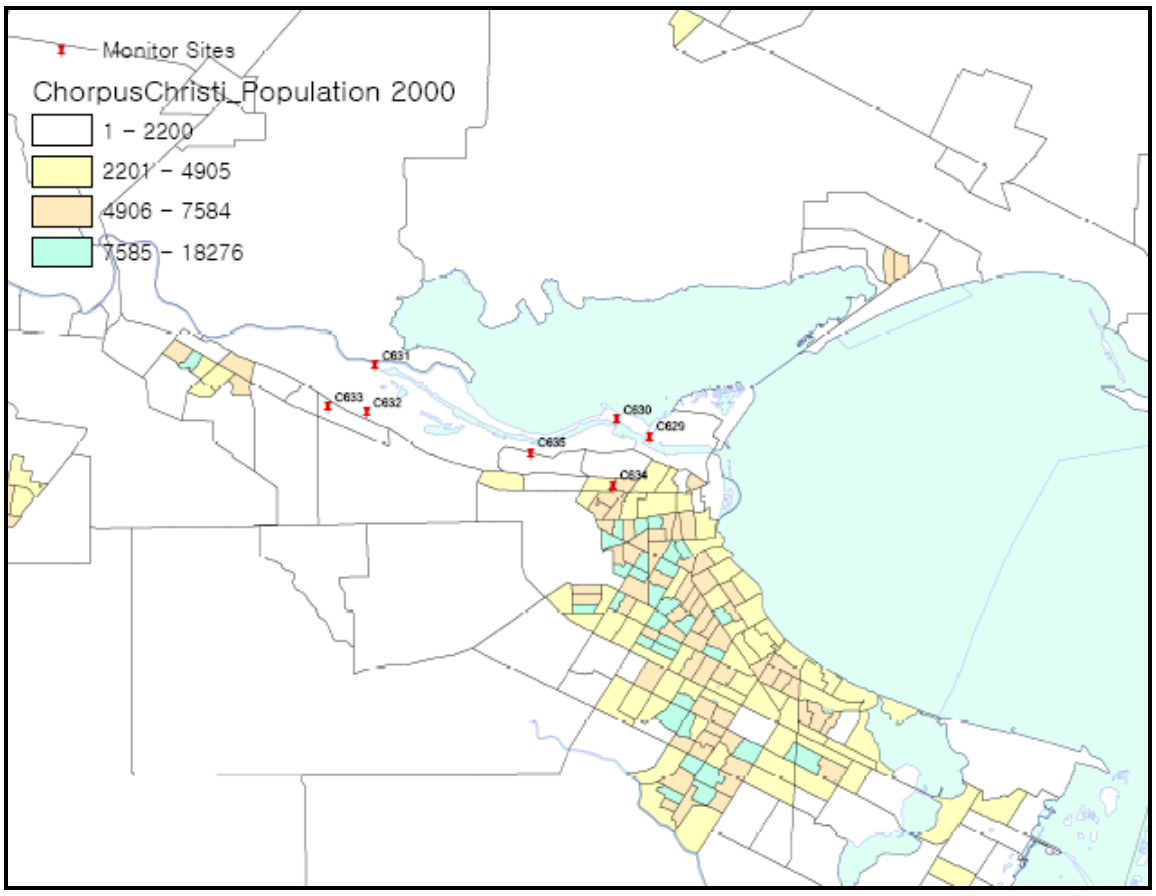

Figure 1.2 Population Densities at Corpus Christi (CENSUS 2000)

Since 2005, The University of Texas at Austin (UT) has operated a dense ambient monitoring network that includes both hourly automated gas chromatograph measurements of multiple hydrocarbon compounds, as well as threshold triggered canister sampling of ambient air (these canister samples can then be analyzed for chemical composition) and meteorological data. These ambient data provide a unique resource to test the ability of current assessments to accurately predict air toxics concentrations.

Atmospheric modeling of air toxics is an integral component of exposure assessment. A need exists to evaluate and inter-compare the modeling tools that are used

in the US with ambient data, in particular in locations where residential development is in close proximity to air toxics emission sources. The seven site network, incorporating both the industrial and residential areas in Corpus Christi, will be used in this work to further the understanding of air quality modeling at a neighborhood scale.

The spatial scale at which air quality modeling is done depends on the nature of the pollutant and its effects. For instance, greenhouse gases impacts are modeled at a global scale. Transport of Saharan dust and large scale wildfires are modeled at a hemispheric or continental scale (Stuart J. Piketh, et al. 2004). At horizontal scales of 4 km to 100 km, ozone, secondary sulfates and nitrates, small fires or regional haze are the principal pollutants of focus in modeling (C. Mensink, 2008). Primary industrial emissions (point sources), vehicle exhaust (on-road mobile source) and other sources that impact pollutant concentrations, in particular air toxics, in very localized areas are modeled at scales below 1 km (neighborhood scale). Modeling air pollutant concentrations at the sub-kilometer level has historically been done using dispersion models, although a variety of new approaches are also under development (Jawad S. Touma, et.al. 2006). The goal of this work is to evaluate the performance of air quality dispersion models in predicting urban to neighborhood scale air toxics concentrations in a mixed urban/industrial environment using ambient data form the Corpus Christi network as a test case.

Scope of Study

This study will discuss the point source emission inventory evaluation, meteorological datasets, and selection of air toxics to be modeled. Comparisons between measured ambient concentrations and predicted concentrations of air toxics using Gaussian dispersion modeling, which represents the current state of practice in the United

States, will be examined for the Corpus Christi area. Predicted air toxics concentrations at gridded and discrete receptors, such as schools and hospitals, will also be presented.

This thesis is structured into six chapters with appendices and references. Chapter 2 will provide a literature review of Gaussian dispersion models types and applications. In Chapter 3, the modeling methodology, including the uncertainties and assumptions, is described along with the performance evaluation of the two models used in this work. Chapter 4 presents the inter-comparison of the two models with performance statistics and comparisons with the results of previous studies. Chapter 5 discusses the spatial and sensitivity studies which will show a hotspot analysis and predicted concentrations at sensitive receptors. Finally, Chapter 6 provides a summary and recommendations for future work.

2 LITERATURE REVIEW

Corpus Christi Ambient Monitoring Network

The Corpus Christi area of interest for this study includes two counties, Nueces and San Patricio, shown in Figure 2.1 (US Census Bureau, 2000). Since October 2, 2003, The University of Texas at Austin has operated seven air monitoring stations in Corpus Christi, shown in Figure 2.2, as part of the Corpus Christi Air Monitoring and Surveillance Camera Installation and Operation Project (CCAQP : http://www.utexas.edu/research/ceer/ccaqp/about_CCAQP.htm). Data collected at one or more monitoring stations include hydrogen sulfide (total reduced sulfur), sulfur dioxide (SO_2), total non-methane hydrocarbons (TNMHC), and meteorological (e.g., temperature, wind speed, wind direction, and relative humidity) measurements. As shown in Table 2.1 hourly measurements of speciated volatile organic compounds (VOCs) are also collected continuously at the Oak Park and Solar Estates monitoring stations using auto-GCs with flame ionization detection. Surveillance cameras are located at both of these sites for identification of visible plumes and other visible indicators of emission events. Data obtained from the monitoring stations are available to the public via the TCEQ website: http://www.tceq.state.tx.us/nav/eq/mon_sites.html

Table 2.1 Descriptions and locations of CCAQP monitoring stations.

Monitor Name	**CAMS #**	**AIRS ID**	Address	**Measurements**
Port Grain	629	48-355-0036	2001B East Navigation Blvd.	Sulfur Compounds, Met, TNMHC
J. I. Hailey	630	48-355-0037	2702B East Navigation Blvd.	Sulfur Compounds, Met, TNMHC
West End Harbor	631	48-355-0038	3149B Suntide Rd.	Sulfur Compounds, Met, TNMHC
FHR Easement	632	48-355-0039	8401B Up River Rd.	Sulfur Compounds, Met, TNMHC
Solar Estates	633	48-355-0041	9122 Leopard St.	AutoGC, Sulfur Compounds, Met, TNMHC, Camera
Oak Park	634	48-355-0035	842 Erwin St.	AutoGC, Sulfur Compounds, Met, TNMHC
Dona Park	635	48-355-0034	5707 Up River Rd.	Sulfur Compounds, Met, TNMHC, Camera

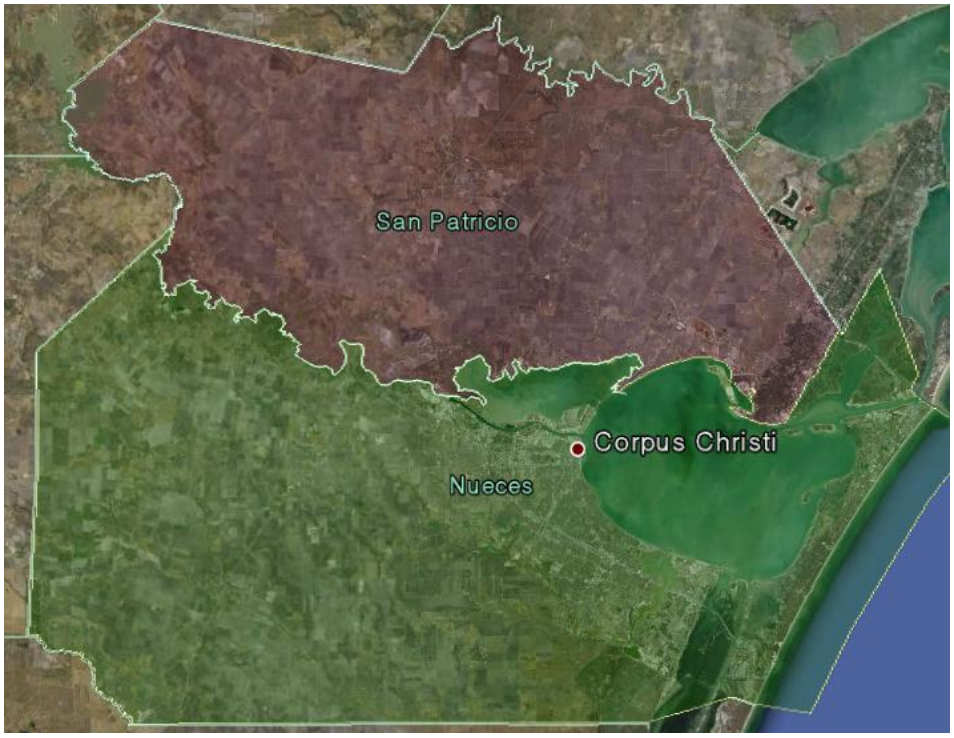

Figure 2.1 Field of interest at Corpus Christi

Figure 2.2 Corpus Christi monitoring stations operated by UT Austin
(Source: http://www.utexas.edu/research/ceer/ccaqp/about_CCAQP.htm)

In addition to the UT network there are several Community Air Toxics Monitoring Network (CATMN) sites supported by TCEQ and Texas A&M - Kingsville (TAMUK). Table 2.2, 2.3 and Figure 2.3 shows the list of these monitoring stations.

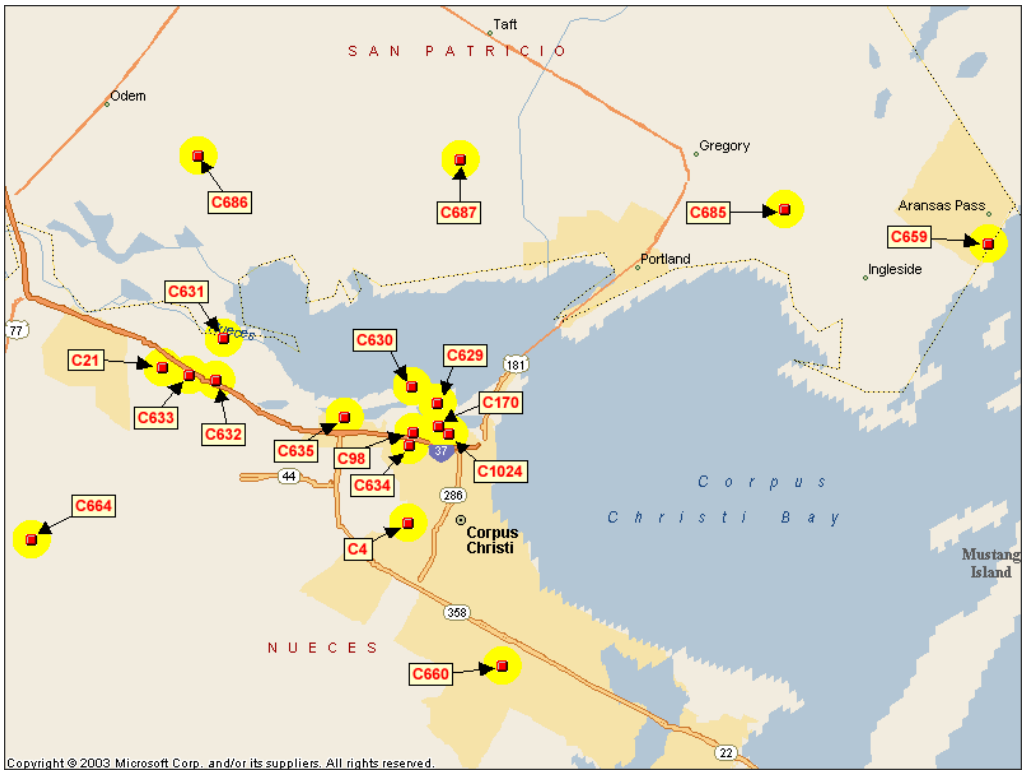

Figure 2.3 Community Air Toxics Monitoring Network locations at Corpus Christi *(Source: http://www.tceq.state.tx.us/cgi-bin/compliance/monops/site_photo.pl?cams=1024)*

Table 2.2 Descriptions and locations of CATMN monitoring stations at Nueces County.

Monitor Name	CAMS #	AIRS ID	Address	Measurements
Corpus Christi West	4	48-355-0025	902 Airport Blvd.	Sulfur Dioxide, Met, Ozone
Corpus Christi Tuloso	21	48-355-0026	9860 La Branch	Sulfur Dioxide, Met, Ozone
Corpus Christi Huisache	98	48-355-0032	3810 Huisache St.	Sulfur Dioxide, Met, Ozone
Corpus Hillcrest	170	48-355-0029	1802 Nueces Bay Blvd.	Met. data
Holly Road	660	48-355-0660	4801 Holly Road	Met, Ozone
Williams Park	1024	48-355-1024	2518 Dempsey Rd.	Met, TNMHC
Violet	664	48-355-0664	3515 FM 1694	Met, Ozone

Table 2.3 Descriptions and locations of CATMN monitoring stations at San Patricio County

Monitor Name	CAMS #	AIRS ID	Address	Measurements
Ingleside	685	48-409-0685	San Patricio municipal water district pumping station off Hwy.361	Met, Ozone
Odem	686	48-409-0686	San Patricio municipal water district pumping station NW of Corpus	Met, Ozone
Taft	687	48-409-0687	San Patricio municipal water district pumping station	Met, Ozone
Aransas Pass	659	48-409-0659	527 Ransom Road	Met, Ozone

Temporal Trends Studied in Corpus Christi Area

McGaughey et al. (2009) developed a conceptual model that examined the factors that influence the concentrations of selected air pollutants at Corpus Christi. McGaughey et al. (2009) focused on Total Non-Methane Hydrocarbons (TNMHC) since there is a continuous record of TNMHC at all of the UT sites, and because refinery emissions consists of large number of hydrocarbon species and TNMHC is a reasonable indicator for total emissions. In McGaughey's report, the average TNMHC concentrations was in the range of 88 ppbC to 441ppbC for the seven CCAQP monitoring stations. The report used a definition of 'high TNMHC concentration' to be 1000 ppbC, and used it as a threshold value for additional analyses because the 98th percentile concentration for all hourly CCAQP measurements collected during the report period roughly corresponds to 1000 ppbC. FHR Easement observed the highest number of hours (2737 hours) of high TNMHC concentration during June 2005- May 2008 period analyzed by McGaughey et al (2009) and Solar Estates showed only 40 hours. Other monitoring stations showed 176~453 hours of 1000 ppbC or greater concentration for TNMHC. McGaughey et al. (2009) also found that higher TNMHC concentrations most often occurred during night

time hours (0000 CST – 0700 CST). And those higher TNMHC concentrations commonly occurred during fall/winter, but were relatively rare during the spring. The seasonal variability of high TNMHC concentrations is likely related, in part, to the seasonal variation in wind direction. Most monitoring stations are characterized by strong wind directionality during higher TNMHC events, suggesting the importance of site-specific emissions sources. For instance higher TNMHC events at Oak Park monitoring station most often occurs with northerly wind component which are most common during the fall/winter seasons, and Oak Park is just south to the refineries (Figure 2.4, adapted from McGaughey et al. 2009; in this Figure the black lines indicate the path of air parcels arriving at the Oak Park site)

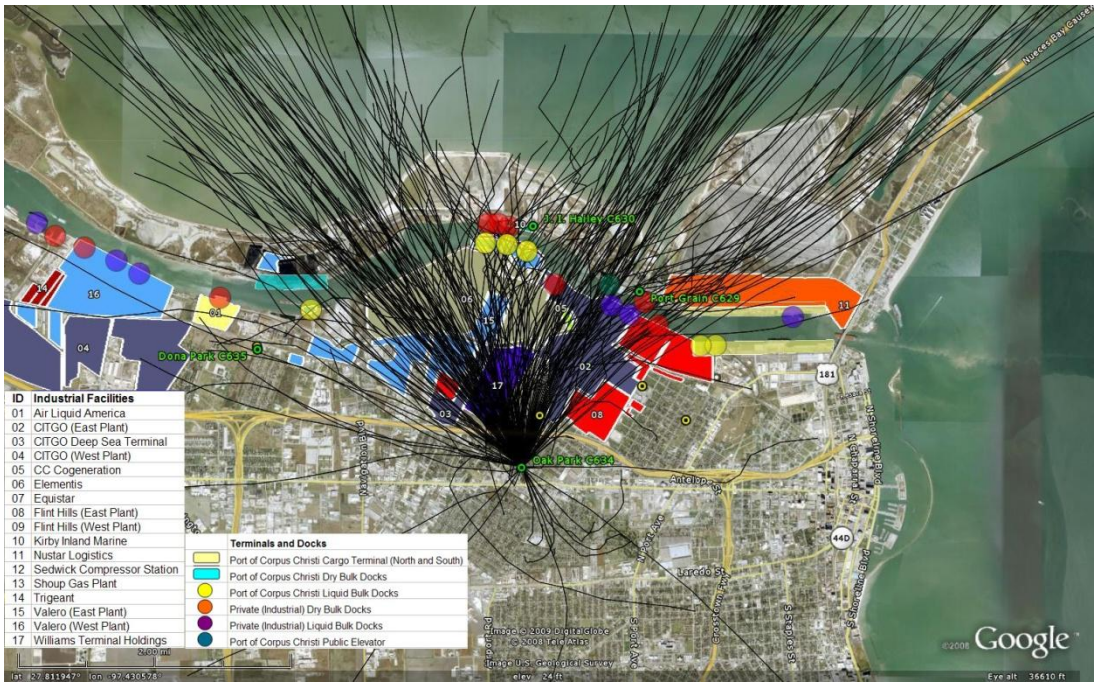

Figure 2.4 Surface back-trajectories as generated by the Corpus Christi Trajectory Analysis Tool for all hours characterized by a TNMHC concentration of 1000 ppb or greater at the Oak Park monitoring station during June 2005 - May 2008.
(Source: Fig. 3-15 from McGaughey et al.2008)

In addition, McGaughey et al (2009) examined benzene concentrations observed at Solar Estates and Oak Park monitoring stations. These sites are equipped with automated gas chromatographs (autoGCs). Other CATMN stations during 1993 through 2008 were analyzed for comparison. Benzene was selected in McGaughey et al. (2009) for these analyses because of the air toxics measured at the Corpus Christi sites; benzene routinely has the highest concentration. The threshold chosen for hours with "high benzene concentrations" was 30 ppbC because this represented approximately the 99th percentile concentration for all hourly CCAQP measurements collected during the report period. Average benzene concentration was 1.93 ppbC at Solar Estates, 3.75 ppbC at Oak Park and 12.02 ppbC at the Huisache station. McGaughey et al. (2009) reports for the two autoGCs for Solar Estates and Oak Park, that the number of hours characterized by benzene concentrations of 30 ppbC or greater is 25 hours at Solar Estates and 473 hours at Oak Park. High concentrations are most frequently measured during the 0400 CST through 0900 CST period, which encompasses both the morning rush hour (high traffic emissions) and periods of low mixing heights (higher concentrations associated with all emissions). At both Oak Park and Solar Estates, the day-of-week analysis demonstrates a weak pattern of lowest concentrations on Sunday in McGaughey et al.'s (2009) report, indicating that the high morning concentrations are due to both increased motor vehicle emissions and low mixing heights. All monitoring stations were characterized by highest concentrations during fall/winter, similar to the TNMHC results.

The diurnal variability of urban or rural VOCs and particulate matter has been described at selected sites or regions of the United States (Singh et al. 1992, Spicer et al. 1996, Bortnick and Stetzer 2002, Main 2002, Judith et al. 1994). Reiss (2006) studied weekly benzene and 1,3-butadiene concentration variation and showed that there are little differences in the weekend-weekday concentrations except during the morning rush hour

at Houston area. For Houston, Reiss (2006) also found that for benzene, winter season concentration was higher than the summer due to higher rates of degradation during summer and other meteorological factors or seasonal difference in emissions. A recent study by McCarthy et al. (2007), used the data obtained from EPA's air quality system (AQS) to analyze diurnal, seasonal, and/or annual variability and trends of hazardous air pollutants. For benzene, it showed morning peaks for the diurnal pattern. McCarthy et al. (2007) also found that winter time benzene concentrations are higher than summer.

Emission Inventory

Emission inventories (EI) are key input data for air quality modeling. McDonald-Buller et al. (2009) assessed each source of air toxics emissions data for the Corpus Christi area. These included data from the National Emission Inventory (NEI), the Toxics Release Inventory (TRI) Program, the State of Texas Air Reporting System (STARS), and the Texas Commission of Environmental Quality's (TCEQ) photochemical modeling emission inventories. Specifically, eleven point source emission inventories were evaluated for Nueces and San Patricio Counties:

1. 2002 TRI
2. 2003 TRI
3. 2004 TRI
4. 2005 TRI
5. 2006 TRI
6. Submittal by the State of Texas to the U.S. Environmental Protection Agency (EPA) for the 2002 Hazardous Air Pollutant (HAP) NEI
7. 2002 U.S. EPA HAP NEI
8. Submittal by the State of Texas to the U.S. EPA for the 2005 HAP NEI

9. 2000 TCEQ Photochemical Modeling EI

10. 2005 TCEQ Photochemical Modeling EI

11. 2008 update to the City of Corpus Christi Emission Inventory prepared by Air Consulting and Engineering Solutions, Ltd. (ACES)

Toxics Release Inventory (TRI) data for toxic air pollutants are submitted and compiled annually and are readily accessible to the public through the U.S. EPA website (http://www.epa.gov/triexplorer). TRI data provide annual records of reported emissions but are summarized only broadly by facilities, which limit the usage for neighborhood - scale air quality modeling when the facilities are large. With the 5 year data of TRI from 2002 through 2006, McDonald-Buller et al. (2009) showed the overall reported benzene emissions in Nueces County have a range from approximately 970 to 1345 tons per year (tpy), and have generally decreased. San Patricio County's reported benzene emissions have varied from 35 to 57 tpy with a recent increase in 2006.

The National Emissions Inventory (NEI) is a comprehensive inventory covering all criteria air pollutants (CAPs) and hazardous air pollutants (HAPs) for all areas of the United States. Complete documentations are available on the following EPA website: http://www.epa.gov/ttn/chief/net/2002inventory.html#documentation. The NEI point source data can be transferred to multiple end-users for a variety of purposes such as compliance demonstrations, emissions trading, and modeling activities. Data elements required for NEI reporting includes more details for site information, such as facility name and address, latitude and longitude, North American Industry Classification System (NAICS) codes, and detailed emission parameters such as emission process data, emission period information, pollutant code, emissions estimate, emission type, control status, and release point ID and location in coordinates.

The TCEQ STARS database and the State of Texas submittal to the NEI contain the same information. According to the TCEQ (Paul Brochi, personal communication, 2008), data that are sent to the U.S. EPA for the NEI are the data that are loaded into STARS as a result of TCEQ's quality assurance process. Annual point source emissions are reported by facilities to the State of Texas using the STARS electronic reporting system. Reporting requirements, emission inventory structure and estimation, and data submission guidelines are described at http://www.tceq.state.tx.us/implementation/air/industei/psei/psei.html. Every site is assigned a unique identification number known as regulated entity reference number (RN). With this RN, McDonald-Buller et al. (2009) was able to match the exact site name and location among the different types of EIs. For the McDonald-Buller et al. (2009) report, the Texas submittal for the 2002 NEI was obtained from Paul Brochi and Ron Thomas of the TCEQ, and the Texas submittal for the 2005 NEI was obtained from EPA web site: http://www.epa.gov/ttn/chief/net/2005inventory.html.

The State of Texas also generates point source emission inventories suitable for photochemical modeling using the STARS database. According to McDonald-Buller et al. (2009), the photochemical modeling inventories have the same level of source resolution as the U.S. EPA NEI and STARS data, but the key difference is that TCQE's air quality modeling group does additional processing to the STARS data such as rule effectiveness and chemical speciation for emissions that are reported in broad categories, such as "unclassified VOCs".

McDonald-Buller et al. (2009) et al. compared the eleven EIs for Corpus Christi. The magnitudes of emissions between the 2002 NEI submittal and the 2002 HAP NEI were identical for most facilities, but had some notable difference in: 1) geographic location disagreement with different state facility identification (SFID) codes, and 2)

different numbers of emission release points (geo-coordinate difference). The report pointed out that the most pronounced difference can be observed between the TCEQ Photochemical Modeling Inventories due to the rule effectiveness and full chemical speciation, whereas the other inventories are only based on reported emissions and emission compositions. This difference was striking with some species showing a factor of 2 to 10 times higher emissions for the 2005 TCEQ Photochemical Modeling Inventory compared to the other inventories. Although substantial differences exist in the magnitude of emissions between the inventories, the relative importance of sites was reasonably consistent for most of the species.

Gaussian Dispersion Modeling

Dispersion models are mathematical models used to predict air pollutant concentrations based on emissions and meteorological inputs, and dispersion and chemical and physical processes within plumes (Holmes et al. 2006). These models typically assume a Gaussian distribution (the bell-shaped distribution) of the plume in the vertical and horizontal directions under steady state conditions and are the most widely used approach for estimating the impact of non-reactive pollutants within 10 kilometers of a source (Turner et al. 2007). A simple Gaussian equation is shown below (Eq. 1a). The concentration χ (Eq.2) is equal to the product of four factors: 1) emission rate, 2) downwind distance in the x direction, 3) distance from the plume centerline in the horizontal (y) direction, and 4) distance from the plume centerline in the vertical (z) direction (Turner et al. 2007).

1) Emissions: Q
2) Downwind factor: $\frac{1}{u}$
3) Crosswind factor: $\frac{1}{\sqrt{2\pi}\,\sigma_y}\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]$
4) Vertical factor: $\frac{1}{\sqrt{2\pi}\,\sigma_y}\left\{\exp\left[-\frac{1}{2}\left(\frac{H-z}{\sigma_z}\right)^2\right]+\exp\left[-\frac{1}{2}\left(\frac{H+z}{\sigma_z}\right)^2\right]\right\}$

Eq.1

$$\chi(x,y,z,H)=\frac{Q}{2\pi\sigma_y\sigma_z}\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]\left\{\exp\left[-\frac{1}{2}\left(\frac{H-z}{\sigma_z}\right)^2\right]+\exp\left[-\frac{1}{2}\left(\frac{H+z}{\sigma_z}\right)^2\right]\right\} \quad \text{- Eq.2}$$

The first factor indicates that concentrations are directly proportional to emission rate. The second factor, which accounts for travel along the plume centerline, has concentrations inversely proportional to the wind speed, u. The Pasquill-Gifford dispersion parameters (Pasquill, 1961; Gifford, 1976), σ_y and σ_z, are functions of two factors: Pasquill stability class and distance from the plume centerline, which depends on the downwind distance. These parameters are used in the third and fourth factors of the Gaussian distribution function. H is the effective height where the pollutant release is taking place.

Although properly applied Gaussian models have useful applications, assumptions inherent in these models can be sources of uncertainty (Turner et al. 2007). Emission rates are generally assumed to be constant and continuous (steady-state emissions) (Weber et al. 1976, Turner et al. 2007). Steady-state meteorology which indicates no variations to wind speed and direction, or Pasquill stability class during transport from source to receptor is another assumption (Turner et al. 2007). Conservation of mass is assumed so all of the effluent remains in the atmosphere, so no allowances are made for loss due to chemical conversion, surface deposition, or removal by precipitation (Turner et al. 2007)

Dispersion modeling was first applied during World War I for military purposes associated with poisonous gas weapons (Turner et al. 2007). As an engineering tool,

dispersion calculations were used to minimize air pollutants from stack emissions (Smith, 1968). Dispersion modeling can also be useful in emergency response planning to reduce the risk to human health or ecological concerns. Finally, modeling often provides an inexpensive alternative to ambient measurements (Turner et al. 2007).

The U.S. EPA's Air Quality Modeling Group (AQMG) conducts modeling analyses to support policy and regulatory decisions in The Office of Air and Radiation (OAR) and provides direction on the full range of air quality models used in assessing control strategies and source culpability (http://www.epa.gov/airquality/modeling.html). In 1978, EPA first issued the Guideline on Air Quality Models to provide consistency and equity in the use of modeling within the U.S. air quality management. The guideline has been periodically revised to ensure that new model developments or expanded regulatory requirements are incorporated (http://www.epa.gov/scram001/dispersion index.htm). These guidelines can be obtained in electronic form via the U.S. EPA Technology Transfer Network Support Center for Regulatory Atmospheric Modeling web page (http://www.epa.gov/scram001/). Using the dispersion models, it is possible to: determine whether a permitted facility is complying with state or federal requirements, assessing where might be the best location to site an air monitor that reads actual data, and so on (MDCA, Citizens' Guide to Air Dispersion Modeling, 2002).

Since 1980, regulatory modeling for impacts of nearby sources (within 20 km) was generally accomplished by using the most recent version of Industrial Source Complex (ISC) Model (U.S. EPA, 1995a: EPA-454/B-95-003a). The latest version of in use is a steady-state Gaussian plume model (ISC3). ISC3 has two versions distinguished as the short term model ISCST3 and the long term model ISCLT3. The major difference between the two was utilizing the wet/dry deposition factor in the calculation (U.S. EPA, 1995b: EPA-454/B-95-003b). The Electric Power Research Institute (EPRI) sponsored a

study to develop and evaluate new, improved plume rise and building downwash algorithms suitable for integration into regulatory air quality model ISCST3, ISC-PRIME (Plume Rise Model Enhancements). ISC-PRIME differs from the original ISC3 as it considers the location of stock, streamlines deflection, calculates the plume rise due to the velocity deficit in wakes or vertical wind speed shear, enhanced calculation for near/far wakes and eliminates discontinuities within the ISC model (Paine et al. 1997: EPRI 1997 TR-2460026). Compared to ISC, it performs better with field data and wind-tunnel data (Paine et al. 1997, EPA 2003: EPA-454/R-03-002). The latest version of ISCST3 was released in February 2002 (http://www.epa.gov/scram001/mcbs/iscst3z9.txt) and a new version of ISC-PRIME (ver. 04269) was released in August 2004 (http://www.epa.gov/scram001/7thconf/iscprime/ iscprime.txt). Calculations for ISC3s models are made for a specific time periods for fixed conditions (steady-state). For the short-term model, calculations are made for hourly time blocks using fixed conditions for one hour. Then conditions are changed, and calculated for the next hour (Turner et al. 2007). Input factors for ISC-PRIME are as follows: wind direction, wind speed, Pasquill stability class, air temperature, and two mixing heights (rural/urban conditions). When considering deposition and depletion factors, additional meteorological parameters, such as friction velocity, Monin-Obukhov length, surface roughness length, precipitation code and rate, are required (U.S. EPA, 1995a: EPA-454/B-95-003a). The ISC-PRIME improved performances were most noticeable in the simulation of ground-level concentrations under stable atmospheric conditions for highly buoyant plumes compared to ISCST3 (Paine et al. 1997). In 1991, the American Meteorological Society (AMS) and the U.S. EPA initiated a formal collaboration group (AMS/EPA Regulatory Model Improvement Committee, AERMIC) with the designated goal of introducing recent advances in boundary layer meteorology into regulatory dispersion models (Paine et al.

2003). Updating ISCST3's algorithms with newly developed modeling techniques (listed below), AERMOD was developed (Turner et al. 2007, Paine et al. 2003). In model performance comparisons, AERMOD found its greatest overall success in reproducing the concentration distributions for buoyant, tall-stack releases in moderate to complex topography compared to ISCST3 (Perry et al. 2005). A more extensive comparison of AERMOD and ISCST3 features is available in EPA's latest AERMOD evaluation (Paine et al. 2003).

Improved algorithms for AERMOD compared to ISC3 (Turner et al. 2007):

1. Dispersion in both the convective and stable boundary layers
2. Plume rise and buoyancy
3. Plume penetration into elevated inversions
4. Computation of vertical profiles of wind, turbulence and temperature
5. The urban boundary layer
6. The treatment of receptors of all types of terrain from the surface up to and above plume height
7. Building downwash

Other efforts were made by Sigma Research Corporation (now part of Earth Tech. INC.) in the mid-1980s to consider both temporal and spatial variations in conditions of the model, which became CALPUFF, a model considering both temporal and spatial variations in conditions (Turner et al. 2007). The CALPUFF users guide shows the full history of model development and is available on web page (http://www.src.com/calpuff/calpuff1.htm).

The U.S. EPA's current generation of dispersion models can broadly be classified in two groups, screening models or refined models. Screening models use simplified calculation procedures designed with sufficient conservatism to allow a determination of

whether a source is clearly not an air quality threat, or whether the source poses a potential threat which could be examined with more sophisticated estimating techniques or measurements (Tai et al. 2008). Major differences between the screening models and refined models are that screening models require fewer input data, and usually use the worst case scenarios (Brode et al. EPA 1988: EPA-450/4-88-010, Touma et al. EPA 1992: EPA-454/R-92-023). More refined models use more detailed inputs (sources, site, weather, terrain, etc). Refined models provide more detailed treatments of physical and chemical atmospheric processes and are more time intensive but theoretically more accurate than the screening models (Turner et al. 2007, Tai et al. 2008). The U.S. EPA currently recommends AERMOD and CALPUFF for the refined models (EPA 2005: Federal Register, EPA 2003: Federal Register). An AERMOD modeling application of primary particulate matter (PM) emissions was recently performed in support of the PM National Ambient Air Quality Standards (NAAQS) proposal (EPA 2010, http://www.epa.gov/ttn/ecas/ria.html). Both models and their performance against ambient measurements are discussed in more detail below.

AERMOD

AERMOD, the successor to the ISC generation of models was introduced by the American Meteorological Society/Environmental Protection Agency Regulatory Model Improvement Committee (AERMIC) in 1991. AERMOD is a near field steady state plume model based on planetary boundary layer (PBL) turbulence structure and scaling concepts, including treatment of both surface and elevated sources over simple and complex terrain (Holmes et al. 2006). It is recommended by the U.S. EPA for examining the effects of sources on receptor that are generally within 50 km of the source (EPA 2005: Federal Register). AERMOD executable program and related documents are

available on EPA web site: http://www.epa.gov/scram001/7thconf/aermod/aermodmep.pdf.

Two pre-processors, AERMAP and AERMET, are required in order to run AERMOD (available on EPA web site: http://www.epa.gov/scram001/dispersion/prefrec.htm#aermod). Figure 2.5 shows the flow and processing of information in AERMOD. AERMAP is a terrain pre-processor which characterizes the terrain and generates receptor grids, discrete receptors, and elevation for AERMOD. Note that in AERMOD, when specifying discrete receptors, it is necessary to specify the position of a source relative to which the receptor is assigned (EPA 2004a, AERMAP user's guide: EPA-454/B-03-003). Gridded terrain data are used to calculate a representative terrain-influenced height (h_c), associated with each receptor location, and are used to calculate the dividing streamline height (EPA 2004a). The gridded data needed by AERMAP is selected from Digital Elevation Model (DEM) data. The elevation for each specified receptor is automatically assigned through AERMAP. For each receptor, AERMAP passes the following information to AERMOD: the receptor's location (x_r, y_r), its height above mean sea level (z_r), and the receptor specific terrain height scale (h_c) (EPA 2004a).

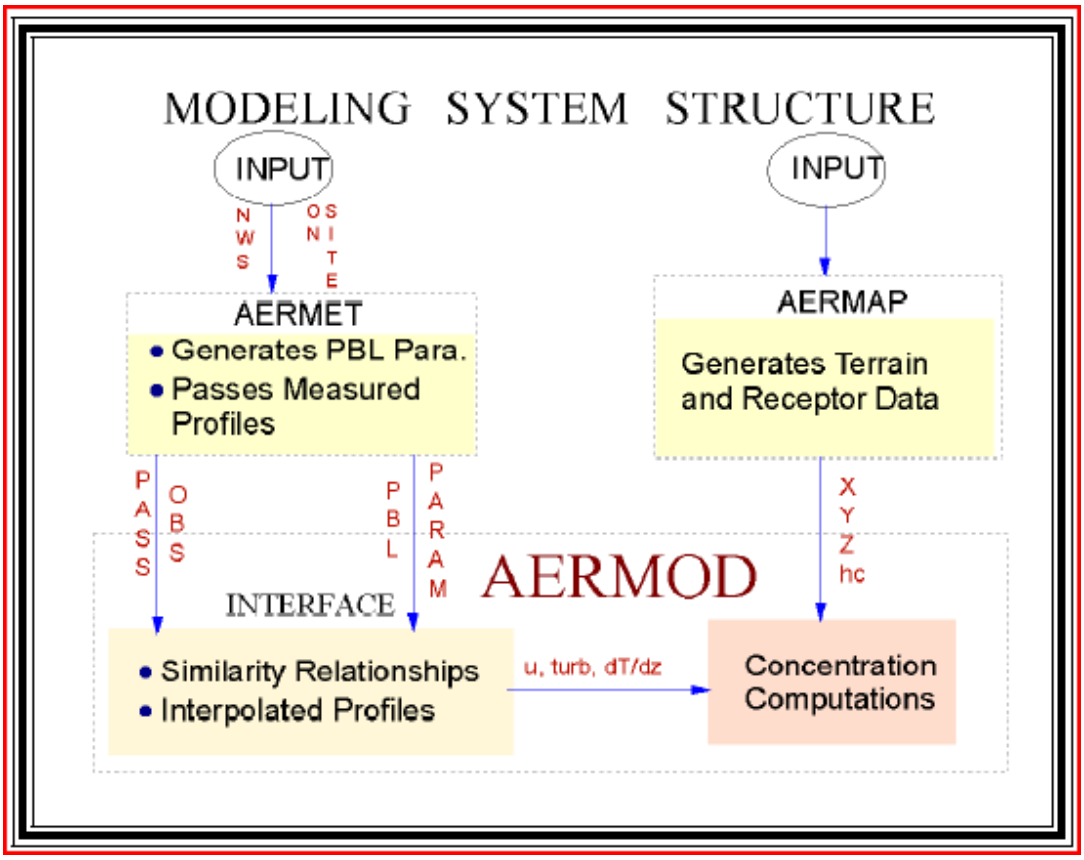

Figure 2.5 Data flow in AERMOD modeling system
(Source: Figure 2. from Cimorelli et al, 2004: EPA-454/R-03-004)

AERMET, the meteorological pre-processor, provides AERMOD with the information needed to characterize the boundary layer parameters and other meteorological data. Surface characteristics, such as Albedo, surface roughness, Bowen ratio (Paine et al. 1987), and other meteorological observations (wind speed, wind direction, temperature, cloud cover: usually available for nearby National Weather Service observations) are input data for AERMET for calculating PBL parameters: friction velocity (u_*), Monin-Obukhov length (L), convective velocity scale (w_*), temperature scale (θ_*), mixing height (z_i), and surface heat flux (H) (EPA 2004b, AERMET user's guide: EPA-454/B-03-002). AERMOD is highly sensitive to the choice

of the on-site meteorological monitor used in the AERMET modeling, as it uses only single values (rather than spatial distributions) for meteorological data (Paine et al. EPA 2003: EPA-454/R-03-003, Faulkner et al. 2008, Long et al. 2004). AERMET is designed to be run as a three-stage process and operates on three types of data: National Weather Service (NWS) hourly surface observations, NWS twice-daily upper air soundings, and data collected from an on-site measurement program (EPA 2004b). The first stage extracts data and assesses data quality. Second stage combines the available data for 24-hour periods and writes these data to an intermediate file. The final stage reads the merged data file and develops the necessary boundary later parameters for dispersion calculations by AERMOD.

Other than the two preprocessors' output, AERMOD needs a runstream setup file which contains the selected modeling options, as well as source location and parameter data, receptor locations, meteorological data file specifications, and output options. AERMOD is able to model multiple sources of different types including point, area and volume sources (Paine et al. 2003). According to AERMOD User's Guide (EPA 2004c: EPA-454/B-03-001), line sources may also be modeled as a string of volume sources or as elongated area sources. Several source groups may be specified in a single run. Source emission rates can be treated as constant throughout the modeling period, or may be varied by month, season, hour-of-day, or other optional periods of variation. Since AERMOD is especially designed to support the EPA's regulatory modeling programs, the regulatory dispersion modeling options, such as stack-tip downwash, and a routine for processing averages when calm winds or missing meteorological data occur, will be the default mode of operation for the model. The user can specify several short term averages to be calculated in a single run of the AERMOD, as well as the overall period (EPA 2004c).

From the evaluation report made by Paine et al. (2003) from EPA, AERMOD provides more realistic characterizations of large buoyant and elevated sources than ISCST3. For the stable boundary layer (SBL), AERMOD assumes the concentration distribution to be Gaussian in both vertical and horizontal. But in the convective boundary layer (CBL), the vertical distribution is described with a bi-Gaussian probability density function (PDF) described by Willis and Deardorff (1981). AERMOD also tracks buoyant plume mass that penetrates the elevated stable layer and allows it to re-enter the mixed boundary layer at some distance downwind (Paine et al. 2003). A complex terrain factor concept of dividing streamline (Snyder et al. 1985) was also included to model buoyant plumes. By this factor the plume is modeled as a combination of terrain-following and terrain-impacting states. This approach has been designed to be physically realistic and simple to implement while avoiding the need to distinguish among simple, intermediate and complex terrain, as required by other regulatory models (Paine et al. 2003). One of the major improvements for AERMOD was to characterize the PBL (Cimorelli et al. 2004: EPA-454/R-03-004) through both surface and mixed layer scaling (Paine et al. 2003). Basic types of printed output available with AERMOD are: summaries of high values (highest, second highest, etc.) by receptor for each averaging period and source group combination, summaries of overall maximum values for each averaging period and source group combination; and tables of concurrent values summarized by receptor for each averaging period and source group combination for each day of data processed. These "raw" concentration values may also be output to unformatted (binary) files (EPA 2004c).

As mentioned earlier, the intended purpose of AERMOD was to replace ISCST3. In 1998, performance evaluation of AERMOD was assessed in various types of environments for which it would be used, and its performance was compared with

ISCST3 (Paine et al. 1998). Minor revisions were being applied at these times, but still AERMOD's performance fit observed data better than ISCST3. Afterwards, AERMOD was proposed by EPA in April 2000 as a replacement for the ISCST3 model (Paine et al. 2003).

Paine et al. (EPA 2003) used the revised version of AERMOD with several model enhancements; including PRIME (Plume Rise Model Enhancements, Schulman et al. 2000) downwash algorithm, complex terrain implementation issues (Cimorelli et al. 2004), options for surface characteristics, and showed improvements over the ISCST3 results, especially for complex terrain situations. By comparison with ISC-PRIME for downwash databases, similar results were found since PRIME algorithms are in both models and should be dominating the dispersion calculations.

Perry et al. (2005) continued the study to see how well AERMOD predicts the high-end (Robust High End Concentration: RHC, Cox et al. 1990), ground-level concentrations that are generally associated with air quality regulations; and estimate if AERMOD's performance could be distinguishably better than that of previous regulatory models. In this study within nonwake situations, AERMOD found its greatest overall achievement, likely believed due to AERMOD's characterization and utilization of the vertical structure of boundary layer in combination with its usage of the dividing streamline concept, in reproducing the concentration distribution for buoyant, tall-stack releases in moderate to complex terrain. In contrast, AERMOD still has some challenges to reproduce some of the lower concentration values with stable conditions. Still, in model-to-model comparison, Perry et al. (2005) concluded that AERMOD's performance surpassed that of ISCST3, and also could present similar results to Hybrid Plume Dispersion Model (HPDM) and Complex Terrain Dispersion Model Plus Algorithms for Unstable Situations (CTDMPLUS) for the special circumstances which these models

were designed for. The evaluation was mainly for point source releases, so there was a need to examine the model's performance for area and volume source types. For this reason, the paper adopted Hanna et al.'s (2001) evaluation for non-buoyant refinery complex (OPTEX database); involving point, line and volume source type emissions, and a non-buoyant release from area and volume source configurations in an open grassy area (Duke forest). At that time, AERMOD had difficulty simulating the dispersion for OPTEX tank source, perhaps because the model was applied before the PRIME algorithm for building downwash. With Perry et al.'s (2005) review, for both OPTEX and Duke Forest's line and volume source conditions, AERMOD showed a good agreement to the observed data.

Similarly, large amount of literature addressed the performance of AERMOD relative to other dispersion models. In Sax et al.'s (2003) study, the importance of the emission characterization was emphasized. Caputo et al. (2003) showed the strong relationship between the meteorological pre-processors for the models. On-site meteorological data input's importance was pointed out to lead to adequate estimates of observed concentrations in urban areas (Venkatram et al. 2004). Hanna et al. (2007) studied the relation of type of emission and site specific conditions to uncertainties. Hanna et al. (2007) stressed the importance of on-road mobile source on model performance. Results of Orloff et al.'s (2006) investigation indicate that when site-specific emission rates are available, air dispersion models can provide reasonably accurate estimates of ambient air concentrations. Kumar et al. (2006), and Zou et al. (2010) provides data that indicate that longer time scale data collection and processing can lead to better performance of AERMOD concentration outputs.

The Clean Air Act Amendments of 1990 (CAAA) requires the U.S. Environmental Protection Agency (EPA) to perform periodic, comprehensive analyses of

the total costs and total benefits of programs implemented pursuant to the Clean Air Act. Recently, part of the prospective study of the benefits and costs of Clean Air Act, a case study for health benefits of benzene reduction in Houston was performed using AERMOD to convert emissions estimates to ambient benzene concentrations in the studied area (http://www.epa.gov/air/sect812/prospective2.html). AERMOD's output data was fed into EPA's Hazardous Air Pollutant Exposure Model, Version 6 (HAPEM6) to generate benzene exposure concentration.

AERMOD was used to estimate sulfur dioxide (SO_2) concentration near residence areas due to refinery point source emissions in Montreal (Smargiassi et al. 2009). Silver man et al. (2007) also adopted AERMOD and ISC model for human health risk assessment, and emphasized the relevant difference between the models for short-term (1-hr averaging) concentrations, due to AERMOD's updated realistic air dispersion processes; such as non-Gaussian dispersion. Odors were also simulated due to ammonia dispersion in farms (Bajwa et al. 2008, Karageorgos et al. 2010).

CALPUFF

CALPUFF was developed by Sigma Research Corporation (currently part of Earth Tech, Inc) sponsored by California Air Research Board (CARB). Use of CALPUFF is recommended by EPA's Guideline on Air Quality Models in Federal Register 2003. The Atmospheric Studies Group (ASG: www. src.com) at TRC provides updates and changes to the model. Files associated with the CALPUFF system, that is, executable/source code, preprocessors, related utilities, test case, and selected meteorological data sets and documents, are available to the public at the TRC web site (http://www.src.com/calpuff/calpuff1.htm). Support documents are available on EPA

web site (http://www.epa.gov/scram001/dispersion_prefrec.htm#calpuff). EPA recommends CALPUFF for the following situations (EPA 2003: Federal Register):

1. CALPUFF is appropriate for long range transport (source-receptor distances of 50 to several hundred kilometers) of emissions from point, volume, area, and line sources. The meteorological input data should be fully characterized with time-and-space varying three dimensional wind and meteorological conditions using CALMET.
2. CALPUFF may also be used on a case-by- case basis if it can be demonstrated that the model is more appropriate for the specific application. The purpose of choosing a modeling system like CALPUFF is to fully treat stagnation, wind reversals, and time and space variations of meteorology effects on transport and dispersion.
3. For regulatory applications of CALMET and CALPUFF, the regulatory default option should be used. Inevitably, some of the model control options will have to be set specific for the application using expert judgment and in consultation with the relevant reviewing authorities.

CALPUFF is a multi-layer non-steady state puff dispersion model designed to model the dispersion of gases and particles using space and time varying meteorology based on similarity equations, turbulence, emission strengths transformation, and removal (Holmes et al. 2006). It uses an integrated puff formulation to simulate four different source types (point, line, area, volume) as inputs (Holmes et al. 2006). A point source is non-geometric dimensional single identifiable emission source such as stacks at power plants. A line source is a one-dimensional source described by mass per time per length of line. There are also cases when designating the source as a two-dimensional area is appropriate, like situations of a forest fire or evaporating emissions from large spill of

volatile liquids. Volume sources can be approximated by a number of area sources stacked in the vertical (EPA 2003: Federal Register, Turner et al. 2007).

A puff model releases emissions periodically (Turner et al. 2007). CALPUFF is intended for use on modeling domains from tens of meters to hundreds of kilometers from a source. It includes algorithms for near-field effects such as building downwash, transitional buoyant and momentum plume rise, partial plume penetration, sub-grid scale terrain and coastal interactions effects, and terrain impingement, as well as longer range effects such as pollutant removal due to wet scavenging and dry deposition chemical transformation, vertical wind shear, overwater transport, plume fumigation, and visibility effects of particulate matter concentrations (Scire et al. 2000a– User's Guide for CALPUFF, Turner et al. 2007). To meet these objectives, the modeling system consists three components: 1) a meteorological modeling package with both diagnostic and prognostic wind field generators; CALMET, 2) a Gaussian puff dispersion model with chemical removal, wet and dry deposition, complex terrain algorithms, building downwash, plume fumigation, and other effects; CALPUFF, 3) post processing programs for the output fields of meteorological data, concentrations and deposition fluxes; PRTMET and CALPOST (Scire et al. 2000a). In addition to CALMET, CALPUFF, and CALPOST, the modeling system interfaces to several other models, which are facilitated by several preprocessors and utilities. An overview of the modeling system is show in Figure 2.6.

In Figure 2.6, there are four models listed which are not included in the CALPUFF system, but they can be interfaced with CALPUFF. MM5/MM4 (Penn State/NCAR Mesoscale Model) is a prognostic wind field model with four dimensional data assimilation (Scire et al. 2000b: CALMET User's Guide). CALMET contains options that allow wind fields produced by MM5/MM4 to be used as an initial guess

field, or pseudo-observations can be used and combined with other data sources as part of the CALMET objective analysis procedure (Scire et al. 2000a). CSUMM (a version of Colorado State University Mesoscale Model) is a primitive equation wind field model (Kessler, 1989) which simulates mesoscale airflow resulting from differential surface heating and terrain effects. CALGRID is an Eulerian photochemical transport and dispersion model, and KSP is a multi-layer, multi-species Lagrangian particle model which can use CALMET outputs (Scire et al. 2000a). The latest CALMET user's guide (Scire et al. 2000b) is available at the following TRC web site: http://www.src.com/calpuff/download/ CALMET/UsersGuide.pdf.

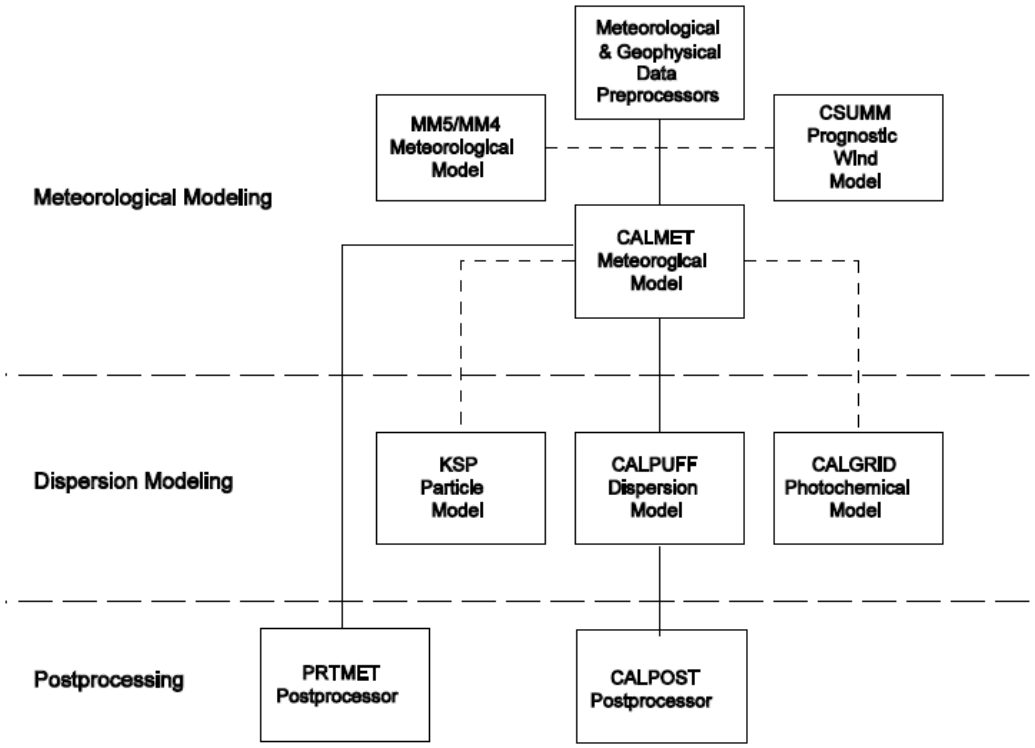

Figure 2.6 Overview of the program elements in the CALMET/CALPUFF modeling system. Also shown are the associated CALGRID photochemical model, the KSP particle model, and the MM5/MM4 and CSUMM meteorological models.
(Source: Figure 1-1 in Scire et al. 2000a)

As mentioned previously, CALMET is a meteorological model which includes a diagnostic wind field generator containing objective analysis and parameterized treatments of slope flows (Mahrt 1982), kinetic terrain effects (Liu and Yocke, 1980), terrain blocking effects (in terms of local Froude number: Allwine and Whiteman, 1985), and a divergence minimization procedure (Goodin et al. 1980), and a micro-meteorological model (Holtslag and van Ulden, 1983) for overland (energy balance method: Holtslag and van Ulden, 1983) and overwater (profile method using the air-sea temperature difference and overwater wind speed) boundary conditions (Scire et al 2000b). When using larger domains, the user has the option to adjust input winds to a

Lambert Conformal Projection coordinate system to account for Earth's curvature. The diagnostic wind field module uses a two step approach to the computational wind fields (Douglas and Kessler, 1988). The first step is an initial-guess wind field for adjusting kinematic effects of terrain, slope flows, and terrain blocking effects. The second step introduces the observational data to produce the final wind field. An inverse-distance squared interpolation scheme is used which weighs observational data heavily in the vicinity of the observational station, white the Step 1 wind field dominates the interpolated wind field in regions with no observational data. The resulting wind field is subject to an optional smoothing and divergence minimization to produce a final Step 2 wind field (Scire et al. 2000b). Prognostic wind field data from the pre-processor CSUMM and MM5/MM4 can also be used as an initial guess or replacement for the Step 1 wind field. Sometimes MM5/MM4 data can be used as an observation in the objective analysis procedure for CALMET. CALMET reads hourly surface observations of wind speed, wind direction, temperature, cloud coverage, ceiling height, surface pressure, relative humidity, and precipitation type codes. Most of the parameters are available from National Weather Service (NWS) surface stations. The preprocessors are designed to use data in National Climatic Data center's (NCDC) standard formats (e.g. CD-144 format for surface data, TD-5600/TD-6201 format for upper air data). The data can also be in free-formatted/user-prepared files for simple-short CALMET runs (Scire et al. 2000b). Table 2.4 summarizes the input data requirements of the CALMET model. CALPUFF is not limited to using meteorological data for a single location, as AERMOD is, but rather wind fields and meteorological parameters are computed across the domain from multiple observation stations adjusted for topography and surface characteristics (Scire et al 2000a, Turner et al. 2007). The data outputs are hourly fields of winds and other meteorological variables on a gridded modeling domain. Three-dimensional fields

of wind speed/direction, and air temperature for surface and aloft grid cells, and two-dimensional fields at the surface of: Pasquil stability class, surface friction velocity u_*, mixing height z_{ic}, Monin-Obukhov length L, convective velocity scale w_*, and precipitation rate are included (Scire et al. 2000b).

CALPUFF is a multi-layer, multi-species, non-steady state puff dispersion model that simulates the effects of time- and space-varying meteorological conditions on pollutant transport, transformation and removal. CALPUFF uses the three-dimensional meteorological fields developed by the CALMET model, or simple, single station winds in a format consistent with the meteorological files used to drive the steady-state Gaussian models like ISCST. However, single station winds should be used with caution since they do not allow CALPUFF to take advantage of its capabilities to treat spatially variable meteorological fields (Scire et al. 2000a). Unlike other steady-state continuous plume models, which do not track the contribution or carryover of plumes from the previous hours, CALPUFF tracks the puffs until they leave the domain, and allows consideration of dynamic wind fields that change spatially and temporally for each puff based on wind fields specified by a grid of values.

Table 2.4 Summary of Input Data Required by CALMET
(Source: Scire et al 2000b)

Surface Meteorological Data

Hourly observation of :
- wind speed
- wind direction
- temperature
- cloud coverage
- ceiling height
- surface pressure
- relative humidity

Hourly precipitation data :
- precipitation rates
- precipitation type code

(part of surface data file)

Upper Air Data

Twice-daily observed vertical profiles of :
- wind speed
- wind direction
- temperature
- pressure
- elevation

Hourly gridded wind fields (optional) :
- MM4/MM5 output
- CSUMM output

Overwater Observations (optional)
- air-sea temperature difference
- air temperature
- relative humidity
- overwater mixing height
- wind speed
- wind direction
- overwater temperature gradients above and below mixing height

Geophysical Data

Gridded fields of :
- terrain elevations
- land use categories
- surface roughness length (optional)
- albedo (optional)
- Bowen ratio (optional)
- soil heat flux constant (optional)
- anthropogenic heat flux (optional)
- vegetative leaf area index

During the calculation of the wind fields, the user selects grid spacing based judgments involving terrain, shoreline, and other surface characteristics. Pollutants

released into the atmosphere will be transported and dispersed by each grid cell's specific wind data. Such transport and dispersion is simulated by the release and transport of circular puffs that grow to simulate the dispersion (Turner et al. 2007). The major features and options of CALPUFF model are summarized in Table 2.5. Some of the technical algorithms are briefly described below (Scire et al.2000a).

- Dry Deposition: A full resistance model, which uses a multi-layer approach by adding the resistance to deposition for each layer, is provided for computation of dry deposition rates of gases and particulate matter as a function of geophysical parameters, meteorological conditions, and pollutant species. Options are provided to allow user-specified diurnally varying deposition velocities to be used for one or more pollutants instead of the resistance model or to bypass the dry deposition completely.
- Wet Deposition: An empirical scavenging coefficient approach is used to compute the depletion and wet deposition fluxes due to precipitation scavenging. The scavenging coefficients are specified as a function of the pollutant and type of precipitation.
- Chemical Transformation: CALPUFF includes options for parameterizing chemical transformation effects using the five species scheme (SO_2, SO_4, NO_x, HNO_3, and NO_3) employed in the MESOPUFF II model (Scire and Insley, 1993), which is a pseudo-first-order chemical reaction model, or a set of user-specified diurnally-varying transformation rates.
- Subgrid Scale Complex Terrain: The complex terrain module in CALPUFF is based on the Complex Terrain Dispersion Model (CTDMPLUS, Perry et al. 1989). Plume impingement on subgrid scale hills is evaluated using a dividing streamline (H_d) to determine which pollutant material is deflected around the

sides of a hill (below H_d) and which material is advected over the hill (above H_d). Individual puffs are split into up to three sections for these calculations.

- Puff Sampling Functions: To solve many of the computational difficulties with applying a puff model to near-field releases, CALPUFF includes a set of accurate and computationally efficient puff sampling routines. In near-field applications during rapidly-varying meteorological conditions, an elongated puff (slug) sampling function is used. An integrated puff approached is used during less demanding conditions to reduce the computational burden.
- Wind Shear Effects: An optional puff splitting algorithm allows vertical wind shear across individual puffs to be simulated. Differential rates of dispersion and transport occur on the puffs generated from the original puff, which in some conditions can substantially increase the effective rate of horizontal growth of the plume.

Table 2.5 Major Features of the CALPUFF Model
(Source: Scire et al. 2000a, Table 1-1)

- **Source types**
  - Point sources (constant or variable emissions)
  - Line sources (constant or variable emissions)
  - Volume sources (constant or variable emissions)
  - Area sources (constant or variable emissions)
- **Non-steady-state emissions and meteorological conditions**
  - Gridded 3-D fields of meteorological variables (winds, temperature)
  - Spatially-variable fields of mixing height, friction velocity, convective velocity scale, Monin-Obukhov length, precipitation rate
  - Vertically and horizontally-varying turbulence and dispersion rates
  - Time-dependent source and emissions data
- **Efficient sampling functions**
  - Integrated puff formulation
  - Elongated puff (slug) formulation
- **Dispersion coefficient (σ_y, σ_z) options**
  - Direct measurements of σ_v and σ_w
  - Estimated values of σ_v and σ_w based on similarity theory
  - Pasquill-Gifford (PG) dispersion coefficients (rural areas)
  - McElroy-Pooler (MP) dispersion coefficients (urban areas)
  - CTDM dispersion coefficients (neutral/stable)
- **Vertical wind shear**
  - Puff splitting
  - Differential advection and dispersion
- **Plume rise**
  - Partial penetration
  - Buoyant and momentum rise
  - Stack tip effects
  - Vertical wind shear
  - Building downwash effects
- **Building downwash**
  - Huber-Snyder method
  - Schulman-Scire method

(Continued)

Table 2.5 (Continued) Major Features of the CALPUFF Model
(Source: Scire et al. 2000a, Table 1-1)

- **Subgrid scale complex terrain**
  - Dividing streamline, H_d:
    - Above H_d, puff flows over the hill and experiences altered diffusion rates
    - Below H_d, puff deflects around the hill, splits, and wraps around the hill

- **Interface to the Emissions Production Model (EPM)**
  - Time-varying heat flux and emissions from controlled burns and wildfires

- **Dry Deposition**
  - Gases and particulate matter
  - Three options:
    - Full treatment of space and time variations of deposition with a resistance model
    - User-specified diurnal cycles for each pollutant
    - No dry deposition

- **Overwater and coastal interaction effects**
  - Overwater boundary layer parameters
  - Abrupt change in meteorological conditions, plume dispersion at coastal boundary
  - Plume fumigation
  - Option to introduce subgrid scale Thermal Internal Boundary Layers (TIBLs) into coastal grid cells

- **Chemical transformation options**
  - Pseudo-first-order chemical mechanism for SO_2, $SO_4^=$, NO_x, HNO_3, and NO_3^- (MESOPUFF II method)
  - User-specified diurnal cycles of transformation rates
  - No chemical conversion

- **Wet Removal**
  - Scavenging coefficient approach
  - Removal rate a function of precipitation intensity and precipitation type

- **Graphical User Interface**
  - Point-and-click model setup and data input
  - Enhanced error checking of model inputs
  - On-line Help files

- Building Downwash: The effects of reduced plume rise and the enhanced dispersion of effluent influenced by structure turbulence are included in current CALPUFF model using the PRIME (Schulman et al. 1997).
- Overwater and Coastal Interaction Effects: Since the CALMET meteorological model contains both overland and overwater boundary layer algorithms, the effects of water bodies on plume transport, dispersion, and deposition can be simulated with CALPUFF. The puff formulation of CALPUFF is designed to handle spatial changes in meteorological and dispersion conditions, including abrupt changes which occur at the coastline of a major body of water.
- Dispersion Coefficients: Several options are provided in CALPUFF for dispersion coefficient computation, including the use of turbulence measurements (σ_v and σ_w), the use of similarity theory to estimate σ_v and σ_w from the modeled surface heat and momentum fluxes, or the use of Pasquill-Gifford or McElroy-Pooler dispersion coefficients, or dispersion equations based on the Complex Terrain Dispersion Model (CDTM)

Input data bases for CALPUFF are summarized in Table 2.6. The meteorological data file contains hourly gridded fields of micro-meteorological parameters and three-dimensional wind and temperature fields. It also contains geophysical data such as terrain heights and land use which are required by both CALMET and CALPUFF model. Emission data inputs can be distinguished by point, line, area, and volume, and once again falls in to two categories, constant or episodic. Hourly observations of ozone data are used in the calculation of SO_2 and NOx transformation rates. Note that for receptor data, CALPUFF includes options for gridded and non-gridded (discrete) receptors. Special subgrid-scale receptors are used with the subgrid-scale complex terrain option. An option is provided for discrete receptors to be placed at ground-level or above the

local ground level (i.e., flagpole receptors). Gridded and subgrid-scale receptors are placed at the local ground level only (EPA 2003: Federal Register). Table 2.7 summarizes the output files of CALPUFF. There are three main output files: concentration, dry fluxes, and wet fluxes.

Table 2.6 Summary of Input Data Used by CALPUFF
(Source: Scire et al. 2000, Table 1-3)

Geophysical Data (CALMET.DAT)

Gridded fields of:
- surface roughness lengths (z_o)
- land use categories
- terrain elevations
- leaf area indices

Meteorological Data (CALMET.DAT)

Gridded fields of:
- u, v, w wind components (3-D)
- air temperature (3-D)
- surface friction velocity (u_*)
- convective velocity scale (w_*)
- mixing height (z_i)
- Monin-Obukhov length (L)
- PGT stability class
- Precipitation rate

Hourly values of the following parameters at surface met. stations:
- air density (ρ_a)
- air temperature
- short-wave solar radiation
- relative humidity
- precipitation type

Meteorological Data (ISCMET.DAT)

Hourly values (standard records)
- wind speed, flow direction
- temperature, stability class
- mixing height (z_i) for rural/urban

Hourly values (extended records)
- surface friction velocity (u_*), Monin-Obukhov length (L)
- surface roughness (z_o)
- precipitation code and rate
- potential temperature gradient
- wind speed profile power-law exponent
- short-wave solar radiation
- relative humidity

(Continued)

Table 2.6 (Continued) Summary of Input Data Used by CALPUFF
(Source: Scire et al. 2000, Table 1-3)

Meteorological Date (PLMMET.DAT)

Hourly values (standard records)
- wind speed, wind direction
- temperature, stability class
- mixing height (z_i)
- turbulence (σ_θ)
- wind speed profile power-law exponent
- potential temperature gradient

Hourly values (extended records)
- precipitation code and rate
- short-wave solar radiation
- relative humidity

Meteorological Data (SURFACE.DAT, PROFILE.DAT)

Hourly values (SURFACE.DAT - standard records)
- mixing height (z_i)
- surface friction velocity (u_*), Monin-Obukhov length (L)
- surface roughness (z_o)

Hourly values (SURFACE.DAT - extended records)
- precipitation code and rate
- short-wave solar radiation
- relative humidity

Hourly values at multiple levels (PROFILE.DAT)
- height
- wind speed (scalar, vector)
- wind direction
- temperature
- turbulence (σ_v/σ_θ, σ_w)

Restart Data (RESTARTB.DAT)

Model puff data generated from a previous run (allows continuation of a previous model run)

(Continued)

Table 2.6 (Continued) Summary of Input Data Used by CALPUFF
(Source: Scire et al. 2000, Table 1-3)

Emissions Data (CALPUFF.INP, PTEMARB.DAT, BAEMARB.DAT, VOLEM.DAT, LNEMARB.DAT)

Point source emissions:

- Source and emissions data for point sources with constant or cyclical emission parameters (CALPUFF.INP)
- Source and emissions data for point sources with arbitrarily-varying emission parameters (PTEMARB.DAT)

Area source emissions

- Emissions and initial size, height, and location for area sources with constant or cyclical emission parameters (CALPUFF.INP)
- Gridded emissions data for buoyant area sources with arbitrarily-varying emission parameters (BAEMARB.DAT)

Volume source emissions

- Emissions, height, size, and location of volume sources with constant or cyclical emission parameters (CALPUFF.INP)
- Emissions data for volume sources with arbitrarily-varying emission parameters (VOLEM.DAT)

Line source emissions

- Source and emissions data, height, length, location, spacing, and orientation of buoyant line sources with constant or cyclical emission parameters (CALPUFF.INP)
- Emissions data for buoyant line sources with arbitrarily-varying emission parameters (LNEMARB.DAT)

Deposition Velocity Data (VD.DAT)

- Deposition velocity for each user-specified species for each hour of a diurnal cycle

Ozone Monitoring Data (OZONE.DAT)

- Hourly ozone measurements at one or more monitoring stations

Chemical Transformation Data (CHEM.DAT)

- Species-dependent chemical transformation rates for each hour of a diurnal cycle

Hill Data (HILL.DAT)

- Hill shape and height parameters in CTDMPLUS format for use in the subgrid-scale complex terrain module (CTSG)

CTSG Receptors (HILLRCT.DAT)

- Receptor locations and associated hill ID in CTDMPLUS format

Subgrid Scale Coastal Boundary Data (COASTLN.DAT)

- File containing X,Y coordinates of subgrid scale coastlines to be treated by CALPUFF

Table 2.7 Summary of CALPUFF Output Files
(Source: Scire et al. 2000, Table 1-4)

Default File Name	Contents	Unit* Number	Type
RESTARTE.DAT	Output restart file containing a dump of all puff parameters sufficient to allow a model run to continue (optional)	IO4	Unformatted
CALPUFF.LST	List file produced by CALPUFF	IO6	Formatted
CONC.DAT	One-hour averaged concentrations (g/m^3) at the gridded and discrete receptors for species selected by the user in the control file (optional)	IO8	Unformatted
DFLX.DAT	One-hour averaged dry deposition fluxes ($g/m^2/s$) at the gridded and discrete receptors for species selected by the user in the control file (optional)	IO9	Unformatted
WFLX.DAT	One-hour averaged wet deposition fluxes ($g/m^2/s$) at the gridded and discrete receptors for species selected by the user in the control file (optional)	IO10	Unformatted
VISB.DAT	Relative humidity data required for visibility-related postprocessing (optional)	IO11	Unformatted
DEBUG.DAT	Tables of detailed puff/slug data useful for debugging (optional)	IO30	Formatted
MASSFLX.DAT	Hourly report of mass flux into and out of regions defined by the boundaries in the FLUXBDY.DAT file	IO36	Formatted
MASSBAL.DAT	Hourly report of changes in mass of all species modeled	IO37	Formatted

* Variable shown is the parameter controlling the FORTRAN unit number associated with the file. Usually, the value assigned to the parameter is consistent with the name (i.e., IO8 = 8). However, the value can be easily changed in the parameter file to accommodate reserved unit numbers on a particular system.

An early version of CALPUFF (version 4.0, level 960612) was compared to ISC3 by EPA (Coulter et al. 1998: EPA-454/R-98-020) using the steady-state meteorological conditions to express true model differences, and variable meteorological conditions for sensitivity studies in plume characteristics or relative performance as a function of distance from the release source. Results showed similar concentrations for steady-state environments, but could produce higher ground level concentrations with CALPUFF for

variable meteorological conditions. Not only the climatological characteristics of a region appear to be a factor, but also the accumulation of hour by hour meteorological conditions on the transport of CALPUFF puffs should be the key to understand the difference between the two models. For the overall trends, CALPUFF simulates higher concentrations than ISC3 for taller point sources, and near-receptor points. This is caused by the ISC3 plume not reaching the ground, or not fully dispersing to the ground, whereas CALPUFF can model effluent dispersion with wind reversals for receptors near the stack base. At more distant downwind receptors, the bias changes direction from CALPUFF yielding higher concentrations, to CALPUFF yielding relatively lower concentrations than that of ISC3's concentrations due to the complex interaction of transport, vertical mixing, and dispersion calculations in CALPUFF. Further scientific evaluation of the model can be found in Allwine et al. (1998) review.

Uncertainty in the wind field is acknowledged as a source of error when applying a dispersion system in an attempt to match measured field data (Chang et al. 2003). Elbir (2003) recently modeled SO_2 concentrations in Izmir (Turkey) air with the CALMET-CALPUFF dispersion model with an accuracy of about 68%. Underprediction might be caused by underprediction of emissions from industrial and domestic heating sources, the influence of surrounding major buildings and street canyons, and uncertainties in the meteorological data, since not all input data were located within the modeling domain. Levy et al. (2003) estimated primary ($PM_{2.5}$) and secondary particulate matter (ammonium sulfate and ammonium nitrate) exposure due to power plant emissions in Georgia by using CALPUFF. The CALPUFF version available at the time of study assumed background concentration of ammonia as constant and spatially uniform, which had less ability to capture ammonia-limited conditions. Other limitations were due to sulfate and nitrate chemistry (Garrison et al., 1999) not considered in CALPUFF. PM10

dispersion was simulated with CALPUFF by Song et al. (2006) for Beijing (China) and Henderson et al. (2008) for British Columbia forest fires. Emission sources used in the Beijing study included electrical generating units, industrial plants, boilers for winter heating, construction plants, and other mobile emissions estimated by U.S. EPA MOBILE6.2 (http://www.epa.gov/oms/m6.htm) and resuspended road dust calculated according to EPA AP-42 (http://www.epa.gov/ttnchie1/ap42. In the CALPUFF model, photochemical reactions were not considered since in winter seasons, Beijing observes low relative humidity and cold temperatures, and the model preformed well compared to the observational data. Henderson et al. (2008) observed poor performance of CALPUFF at predicting smoke in low and moderate wind conditions where CALMET performance is known to be poor (Burkholder 2005).

A study of windblown dust within the Mexico City Basin was performed by Villasenor et al. (2003) and showed reasonable agreement between CALPUFF modeled and observed data. Villasenor et al. (2003) concluded that differences between the model and observation were due to the different dust sources within the vicinity of the receptors. CALPUFF is often used to estimate population exposure for fine particulates from power plants (Zhou et al. 2003, Levy et al. 2003, and Lopez et al. 2005). All studies showed the importance of background concentration of ammonia in forming secondary particles. Other than industrial source, Gilliam et al. (2005) used CALPUFF plume model to calculate the $PM_{2.5}$ dispersion after the collapse of the New York Trade Center towers on 11 September 2001, estimating the tower as a volume source. Limitations in this research included: 1) extremely non-homogeneous surface around lower Manhattan, and 2) relatively coarse time step (1 hour), where significant variations in the boundary layer structure is in many circumstances considerably less than one hour for such complex region. CALPUFF is also used for deposition modeling. Vitt et al. (2003) used

CALPUFF to calculate nitrogen deposition which can influence sensitive ecosystems, and Pfender et al. (2006) studied dispersal of fungus spores from grass-seed fields infested with the stem rust fungus. Long-term deposition of hazardous heavy metal materials (cadmium, lead, and zinc) were characterized by CALPUFF (MacIntosh et al. 2010). MacIntosh et al. (2010) compared the results with measured data from soil and attic dust within the model domain and found good agreement, concluding that CALPUFF is expected to be reliable for long-term average ambient concentration modeling, since deposition estimates are linear to air concentrations.

Neighborhood Scale Air Quality Modeling

Accurate performance of air quality simulation models at fine (~1 km or less) scales will be needed for performing exposure and risk assessments in urban areas (Ching et al., 2004). As the modeling domain gets into smaller scales, characterizing concentrations of pollutants in selected microenvironments will occupy a prominent position. For example, Zhu et al (2009) found elevated concentrations of ultrafine particles near three roadways in Central Texas with a return to background levels within several hundred meters; Clements et al. (2009) found evidence of chemical processing of NO_x near roadways other than atmospheric dilution. In the same study, Denbleyker (2008) used a roadway plume dispersion model (CALINE4) to predict concentrations of CO and NO_x near roadways by using emission factors produced by MOBILE6, and found lower concentration predictions which are not consistent with observations, suggesting that near-source mixing at roadways has more complex behavior than a dispersion factor alone. Cohen et al. (2005) characterized the relationship between motor vehicle emissions and ambient concentrations of 1,3-butadiene, benzene, and diesel PM with CALPUFF

showing the steep spatial gradients along roadways in Portland, with a zone of influence somewhere between 200 and 400m.

These studies indicate that a resident in contiguity with a roadway and a resident couple of blocks away might have extremely different air quality situations. Although dense ambient monitoring networks are ideal to evaluate air quality model performance, resources for such efforts are generally limited. Periodic air sampling air at fixed sites has been commonly used, but time and resource constraints have meant that only sparse sampling grids could be utilized (Kolb et al. 2004). Therefore, Kolb et al. (2004) and Herndon et al. (2005) suggested use of a mobile lab with rapid response instruments for real-time measurements of urban pollutants in a finer spatial resolution since understanding the spatial gradients of air toxics plays a key role in emission source characteristics (EPA 2009: Air Toxics Data Analysis Workbook). In particular, Chow et al. (2002) noted that monitoring of air toxics for long-term averages need less frequent samples than monitoring for extreme events. And for short-term experiments involving spatially dense measurements and modeling may assist in making or verifying judgmental sampling locations (Nesbitt and Carter, 1996) which can reduce the burden.

Other than direct measurement of ambient air, several types of refined air quality modeling approaches can be applied. Gaussian models are heavily dependent on the spatial allocation and rate of emissions and meteorological inputs (Sax et al. 2003), which are not always available. Isakov and Venkatram (2006) performed a case study at Wilmington, CA to resolve issues when processing neighborhood scale air toxic modeling. The author emphasized that incorporating site-specific data can lead to improvement in modeling concentration estimates. Also in this case study, uncertainty analysis suggests that point estimates at case study receptors could be substantially biased because of the potential for uncertainty in on-road emissions estimates. Venkatram et al.

(2009) showed the suitability of AERMOD for predicting the concentrations of VOCs (benzene, 1,3-butadiene, and toluene) at high spatially resolved intervals from 10 to 100m from the nearest travel lane of highway in Raleigh, North Carolina. Venkatram et al. (2009) used a three step process: 1) determine uncertainty in the model estimates by evaluating dispersion model estimates with 10-min averaged NO -data measured from edge of the road during field study, 2) use dispersion model estimates and their uncertainties determined in step 1, to construct pseudo-observations, 3) Fit pseudo-observations to actual observations of VOC concentrations measured during the field study. This process provides estimates of the contribution of traffic emissions to the VOC concentrations and also provides estimates of emission factors and background concentrations of the VOCs. With these efforts, the performance of AERMOD by this research in explaining near-road concentrations supported its use in estimating less-than-100m scale impacts of traffic emissions in the absence of concentration measurements. Since dispersion models depend on meteorological input data, people introduce hybrid models. Isakov et al. (2007) tried to improve the model performance using comprehensive prognostic meteorological models, such as MM5 and Eta model (the National Centers for Environmental Prediction's North American Mesoscale Model). In this study, MM5 and Eta data had the advantage for coastal zones and complex terrain where original methods (NWS data, on-site measurement) are not reliable.

An alternative method to the above dispersion models is *Land use regression model (LUR)*. Land use regression model has been utilized to characterize air pollution exposure and health effects for individuals residing within urban areas (Patrick et al. 2007). The model uses monitored pollutant concentrations as the response variable and a comprehensive set of land use, physical geography and transportation variables as predictors (Briggs et al. 2000). In LUR models, Geographic Information Systems (GIS)

are usually used to integrate data from land use, transportation and physical geography to derive a land use regression prediction model of the ambient air (Corburn et al 2007, Moore et al. 2007). Land use regression models are usually calibrated with NO_2 as a marker for traffic exposure (Moore et al 2007). Regardless of the inherent toxicity or danger of chronic NO_2 exposure, its ubiquitous association with vehicle exhaust makes it a convenient tracer for overall level of exposure to related pollutants. In addition, NO_2 is unique in that accurate, low-cost measurement techniques exist. As a result, mapping or modeling of NO_2 on the urban scale is increasingly being pursued for the purpose of epidemiological surveys and risk assessment (Mavco et al. 2008).

There are also comprehensive neighborhood air quality studies like the Barrio Logan Air quality study (2004) conducted by California Environmental Protection Agency. The project started from ambient air monitoring to investigate local-scale hot spots or pollution gradients. Micro-scale modeling by AERMOD was verified by a tracer study and showed over-prediction in near field and under-prediction at distances away. CALGRID/CALMET was used for regional photochemical modeling. The regional model was successful in simulating emissions distributed in the domain or pollutants generated by secondary reactions, but for few localized emitted sources, the regional models were not appropriate.

Overall, in neighborhood scale air toxic modeling, there are needs for accurate emission inventories and meteorological data sets. Site specific observation data will help evaluate model performance. Corpus Christi has a mixed urban/industrial environment resulting in close proximity of the petroleum refining complex to residential neighborhoods which raises concerns of exposure to air toxics. For the past three years, UT has operated a dense ambient monitoring network that includes both hourly automated gas chromatographs as well as threshold triggered canister samples and

meteorological data. A Photochemical Modeling Inventory is available for this region which provides specific point emission locations and emission amounts. The monitoring network and emission inventory, incorporating both the industrial and residential areas in Corpus Christi, provides a unique opportunity to evaluate the two U.S. EPA preferred air toxic model, AERMOD and CALPUFF, at the neighborhood-scale level. These models, in their current form, have not been intercompared with this density of observational data for concentrations and meteorology. Major objective to this thesis are to;

- Estimate spatial and temporal distributions of concentrations for benzene in Corpus Christi using AERMOD and CALPUFF at selected date
- Compare the predictions from AERMOD, CALPUFF, and observed concentration
- Identify benzene hotspots and predict concentrations for sensitive receptors (schools, hospitals, etc)

The modeling methods to be used in the analyses, along with the uncertainties and assumptions will be described in the following chapter.

3 Modeling Methods

In this work, AERMOD and CAPUFF predictions will be compared to observations at the Oak Park monitoring site in Corpus Christi. The Oak Park monitoring station (EPA site number: 48-355-0035) was selected for this work since it is located in a region of high population density (Figure 1.2, 3.1), and near major refineries (Figure 3.1). The Oak Park monitoring station is equipped with automated gas chromatographs (autoGCs) that continuously analyze for approximately 55 VOC compounds including benzene. McGaughey et al. (2009) investigated back trajectories of wind patterns and observations of during periods of high TNMHC concentrations (defined as 1000ppbC or over) at Oak Park, which suggested the importance of emission source areas to the north-northeast and north-northwest of Oak Park. The highest TNMHC concentrations occur during the night and early morning hours during the fall and winter. October 1st to November 30th, 2006 was selected for the modeling time period. Benzene was selected as the modeled pollutant because of the importance to air quality in Corpus Christi associated with emissions from Ship Channel industrial facilities, notably the petroleum refining industry, and the recognized importance of benzene concentrations to human health risk and exposure assessments. McGaughey et al. (2009) defined high benzene concentration to be 30 ppbC or over and observed 473 hours of high benzene concentrations at the Oak Park monitoring station during the June 2005 till May 2008 observation period. . McGaughey et al. (2009) also stated that the high concentration was most frequent during 0400 CST through 0900 CST periods, which represent the morning rush hours and periods of low mixing heights. Benzene emission source characteristics including; 1) emission rates (total of approximately 260 tons per year for 2005 TCEQ Photochemical Modeling Inventory), 2) stack height, 3)

stack exit temperature, 4) exit velocity, and 5) stack diameter (EPA 2004c), for modeling were obtained from the 2005 TCEQ Photochemical Modeling inventory (McDonald-Buller et al. 2009).

AERMOD

The AERMOD modeling system consists of one main program (AERMOD) and three pre-processors, AERSURFACE, AERMAP and AERMET (EPA 2004c). Tai et al. (2009) developed the AERMOD modeling configuration used in this work and briefly described below.

AERSURFACE is the preprocessor used to process land cover data to determine the surface characteristics (i.e., albedo, Bowen ratio and surface roughness) for use in the meteorological preprocessor, AERMET. AERSURFACE was not run for this study. Instead, Tai et al. (2009) used the Texas Commission on Environmental Quality (TCEQ) recommended values for albedo (0.18) and Bowen ratio (0.75) for San Patricio County. The surface roughness value was set to 1.0 by Tai et al. (2009), which is indicative of typical urban/industrial areas.

Figure 3.1 Oak Park monitoring station and petroleum refineries outlined in yellow

AERMET is used to calculate PBL parameters (friction velocity, Monin-Obukhov length, convective velocity scale, temperature scale, mixing height, and surface heat flux), based on input surface characteristics from AERSURFACE, as well as standard meteorological observations (wind speed, wind direction, temperature and cloud cover). The current regulatory version of AERMET (Version 06341), which is available from the EPA's web site located at http://www.epa.gov/scram001/dispersion_related.htm was used by Tai et al. (2009). AERMET requires an input runstream file, which directs the actions of AERMET, and meteorological observations, and can be found in Tai et al. (2009). The following surface, upper air and on-site meteorological data were used in the AERMET processing for the period from October 1st through November 30th, 2006.

- Surface: Corpus Christi International Airport (12924) TD-3505 (Integrated Surface Hourly Data) format

- Upper Air: Corpus Christi International Airport (12924) FSL (Forecast Systems Laboratory) format
- On-site : Solar Estates and Oak Park meteorological monitors

AERMAP is the terrain preprocessor for AERMOD. AERMAP determines the terrain base elevation for each receptor and source and calculates the hill height scale value (*hc*) for each receptor. The hill height scale value is used by AERMOD to calculate the critical dividing streamline height (Hc). AERMAP requires an input runstream file, which directs the actions of AERMAP, and digital terrain data. In this study 46 digital elevation model (DEM) files were used to cover the modeling domain. The 7.5-minute North American Datum of 1927 (NAD27) format with 30 meter resolution was selected by Tai et al. (2009). The DEM data files are available from either of the following web sites: http://www.mapmart.com or http://www.webgis.com. The specific DEM files used to cover the modeling domain are listed in the AERMAP input runstream file, which is available at Tai et al. (2009). Discreet sensitive receptor locations were provided by UT to ENVIRON in Geographic coordinate system (GCS), which were assumed to be in North American Datum 1983 (NAD83). Source locations, in GCS coordinates, were taken from the 2005 TCEQ Photochemical Modeling inventory. In addition to the discreet sensitive receptors, a Cartesian grid of receptors with four kilometer grid spacing was output for quality assurance and contour mapping purposes for hourly benzene concentration.

AERMOD uses planetary boundary layer (PBL) parameters calculated by AERMET and the hill height scale (*hc*) determined by AERMAP to calculate the critical dividing streamline height (H_c) (EPA 2004a). AERMOD uses a Gaussian distribution in the horizontal direction, but uses a bi-Gaussian probability distribution function (PDF) in the vertical direction (Willis and Deardorff, 1981). The current regulatory version of

AERMOD (Version 07026) was downloaded from the EPA's web site located at http://www.epa.gov/scram001/dispersion_prefrec.htm#aermod by Tai et al. (2009) and was used in this study. To determine sensitivity of the meteorology input, AERMOD was run twice using AERMET files generated with the Solar Estates On-site monitoring station's meteorological data and once with the Oak Park On-site meteorological monitoring data. Several other control options developed by Tai et al. (2009) and used in this study are defined as below:

Control Options

- Terrain: Elevated (AERMAP processing)
- Pollutant: Benzene (Source characteristics obtained from 2005 TCEQ Photochemical Modeling Inventory) and dry deposition parameters selected by Tai et al. (2009) from User's Guide for the Emissions Modeling System for Hazardous Air Pollutants Version 2 (Strum et al. 2002: EPA 454/B-02-001)

  Diffusivity in air (D_a): 0.08962 cm^2/s

  Diffusivity in water (D_w): 104,000 cm^2/s

  Cuticular resistance (r_{cl}): 25,100 s/cm

  Henry's Law Constant: 557 $Pa\text{-}m^3/mol$
- Averaging Periods : 1-hour, 8-hour
- Dispersion Options : Concentration, Deposition
- Season Definition (GDSEASON) : Seasonal Category 2 (Autumn with unharvested cropland) : September, October, November
- Land Use Category (GDLANUSE) : 5 (suburban areas, grassy)
- Output Units(DEPOUNIT) : g/m^2

Source Data (Emission Inventory)

As described in earlier Chapters, the 2005 TCEQ photochemical modeling inventory obtained from the TCEQ was used for this study.

CALPUFF

CALPUFF is a non steady-state Lagrangian puff model based on the Gaussian dispersion equations (Scire et al. 2000a). CALPUFF can handle complex terrain algorithms, land/water interaction effects, dry and wet deposition, basic chemistry, and building downwash (Scire et al. 2000a). Inputs include CALMET meteorological fields, emissions, and a list of discrete and/or gridded receptors. CALPUFF model development and sensitivity tests were conducted by Tai et al. (2009) at ENVIRON to find the most reasonable configuration for the Corpus Christi domain, which was then used to simulate the October 1st to November 30, 2006 episode. Desirable CALMET options were determined by Tai et al. (2009). Options selected include: the use of high-resolution coastline data, terrain kinematics, additional smoothing aloft to help reduce the magnitude of the vertical velocity, and using micrometeorological variables to compute dispersion coefficients. Table 3.1 and 3.2 specify the final configuration for CALMET and CALPUFF developed by Tai et al. (2009).

Performance Evaluation

AERMOD and CALPUFF model predictions are compared to observed benzene concentrations from the auto-GC at the Oak Park monitoring station. Observed concentrations of benzene from the autoGC have units of ppbc (part per billion Carbon). AERMOD and CALPUFF output results in units of g/m^3, so the simulated outputs

were converted to ppbc for comparison to the auto-GC measurements, assuming a temperature of 25^{o}C and pressure of 1013.25 mb (1 atm) assuming benzene as ideal gas.

Comparisons between predicted and observed concentrations will be evaluated using time series plots, comparisons of daily maximum peak concentrations. Northerly wind binned concentrations, further binned by wind speed will also be studied since residential areas are located south of the industrial area. For large differences between observation and predicted maximum concentrations, back trajectories of wind direction and speed will be analyzed using Christi Trajectory Analysis Tool. Statistical analyses such as weekly/monthly Mean Normalized Growth Errors (MNGE) and Mean Normalized Bias (MNB) (Tesche et al. 1991) will be used to evaluate the performance of each model.

Table 3.1 Final configuration for CALPUFF

Description	Variable	Option selected
Model selection variable	IWFCOD	1. Diagnostic wind module
Compute Froude number adjustment	IFRADJ	1. Yes
Compute kinematic effects	IKINE	1. Yes
Use O'Brien procedure	IOBR	0. No
Compute slope flow effects	ISLOPE	1. Yes
Extrapolate surface wind observations to upper layers	IEXTRP	-4. Similarity theory used, ignore layer 1 at upper air stations
Extrapolate surface winds when calm	ICALM	0. No
Layer-dependent biases	BIAS	-1,9*0 (-1 = no upper air station influence; 0 = weigh surface and upper air stations equally)
Use MM5 as input to CALMET	IPROG	0. No
Use varying radius of influence	LVARY	F
Max radius of influence over land in layer 1	RMAX1	75 km (no default)
Max radius over land aloft	RMAX2	75 km (no default)
Max radius over water	RMAX3	100 km (no default)
Min radius of influence in wind field interpolation	RMIN	0.1 km
Radius of influence of terrain features	TERRAD	1 km
Relative weighting of first guess field and obs in layer 1	R1	10 km (no default)
Relative weighting of first guess field and obs aloft	R2	25 km
Max divergence in divergence minimization procedure	DIVLIM	5.0E-6
Max number of iterations for div. Minimization	NITER	50
# passes in smoothing	NSMTH	6 (layer 1), 6 aloft
Max # stations in each layer for interpolation of data to a grid point	NINTR2	99 for all layers
Critical Froude number	CRITFN	1.0
Empirical factor for kinematic effects	ALPHA	0.1
# of Vertical Layers	NZ	14
Buoy location		300,-1360
Coast line data		Improved coast line data

Table 3.2 Final configuration for CALPUFF

Description	Variable	Option Selected
Emission Inventory		2005 TCEQ Modeling EI
CALMET Run Set #		Run 14
dispersion coefficients		micrometeorological variables used to compute coeff.
Vertical distribution in near field	MGAUSS	1 = Gaussian
Terrain adjustment method	MCTADJ	3 = partial plume path adjustment
Subgrid scale complex terrain	MCTSG	0 = not modeled
Near-field puffs modeled as elongated slugs	MSLUG	0 = no
Transitional plume rise modeled	MTRANS	1 = yes
Stack tip downwash	MTIP	1 = yes
Method for building downwash	MBDW	2 = PRIME method (not default)
Vertical wind shear modeled above stack top	MSHEAR	0 = no
Allow puff splitting	MSPLIT	0 = no
Chemical mechanism flag	MCHEM	0 = no chemistry (not default)
Wet removal modeled	MWET	1 = yes
Dry deposition modeled	MDRY	1 = yes
Gravitational settling	MTILT	0 = no
Method to compute dispersion coefficients	MDISP	3 = PG dispersion coefficients
PG sigma-y,z adjustments for roughness	MROUGH	0 = no
Partial plume penetration of elevated inversion	MPARTL	1 = yes
Strength of temperature inversion from PROFILE.DAT	MTINV	0 = no (computed from measured/default gradients)
PDF for dispersion when convective	MPDF	0 = no

4 MODEL EVALUATION AND INTER-COMPARISON

Observation Benzene Concentrations at Oak Park

Benzene concentrations measured by the University of Texas at the Oak Park monitoring station are archived by the TCEQ (http://www.tceq.state.tx.us/cgi-bin/compliance/monops/agc_daily_summary.pl?user_site=32).

Figures 4.1 and 4.2 show observed benzene concentration from October 1st to November 30th, 2006 by wind direction and wind speed. Since high concentrations are often associated with emission sources located to the north of Oak Park, winds were categorized into five northerly directions and one 'other' category. Winds from the NNE were generally associated with the highest concentrations of benzene at Oak Park. Observed concentrations decreased with wind speed for most wind directions, but stronger winds from the NNE direction were associated with higher elevated concentrations. It was also interesting to find that for very high wind speeds from the NW direction, the concentration of benzene didn't approach zero. The vertical lines on Figure 4.1 indicate Sunday. Concentration differences between weekends and weekdays were not easily distinguishable with the observed data, which is consistent with the findings of McGaughey et al. (2009).

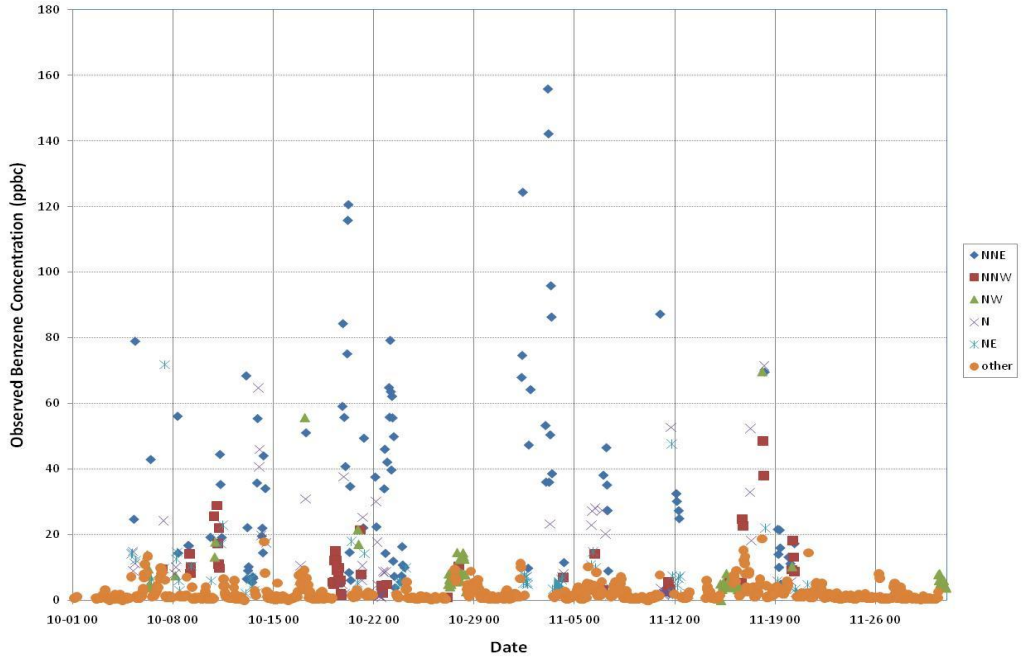

Figure 4.1 Time series of observed benzene concentration at Oak Park by wind direction

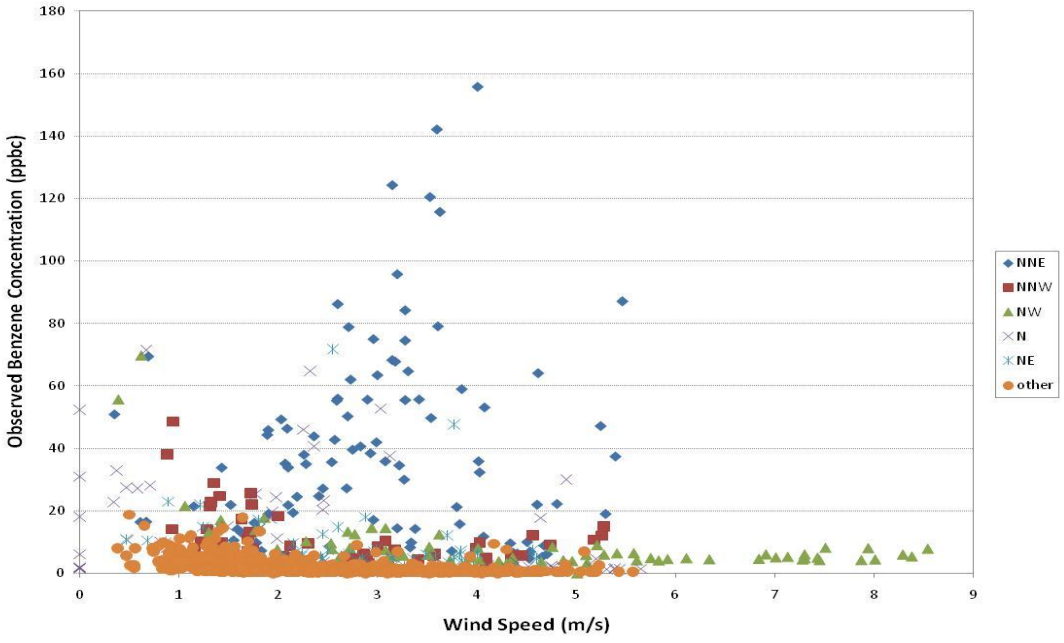

Figure 4.2 Relation to wind speed of observed benzene concentration at Oak Park

Comparisons of Observed and Predicted Benzene Concentrations

AERMOD

The combined meteorology data using the surface data from the NWS station located at the Corpus Christi International Airport (12924) and the on-site meteorological monitor at Oak Park (C634) was processed through AERMET and used as input for AERMOD. Figure 4.3 and 4.4 shows the AERMOD simulated benzene concentrations' time series by wind direction and wind speed observed at the Oak Park monitoring station. Predicted concentrations show higher benzene concentration with northerly wind directions, but could not replicate the high concentrations with higher wind speeds when flow was from the NNE.

Figure 4.5 shows the scatter plots of the simulated concentrations of benzene at Oak Park compared to the observed data at Oak Park binned by wind direction. AERMOD does not replicate the high observed concentrations during higher wind speeds from the NNE direction (Figure 4.6).

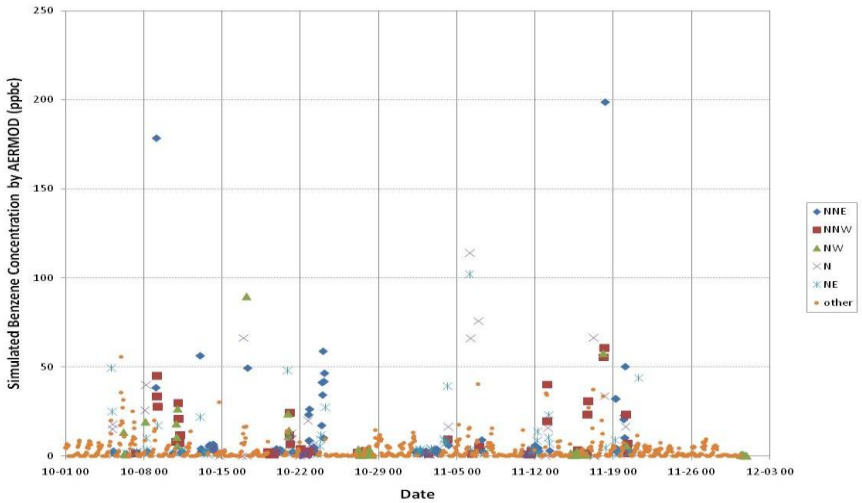

Figure 4.3 Time series of AERMOD simulated benzene concentration at Oak Park by wind direction

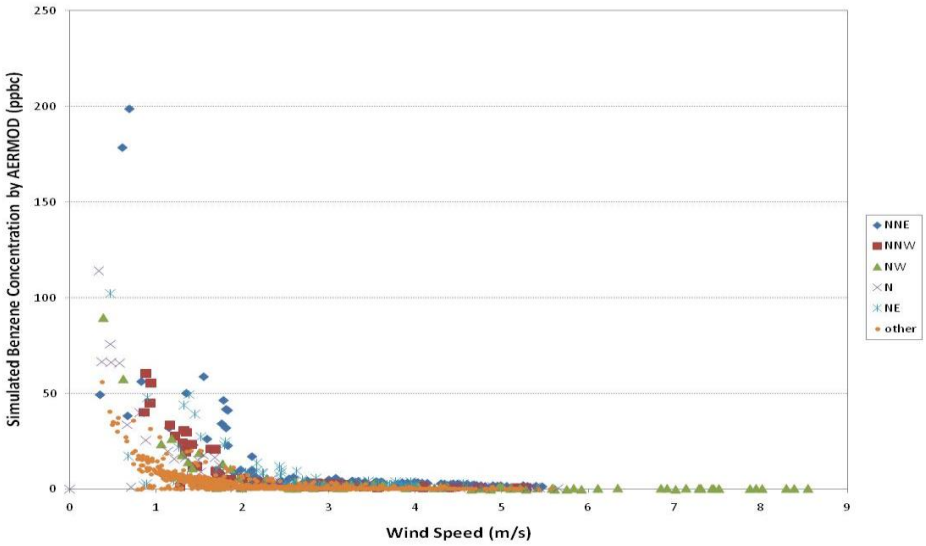

Figure 4.4 Relation to wind speed of simulated benzene concentration by AERMOD at Oak Park

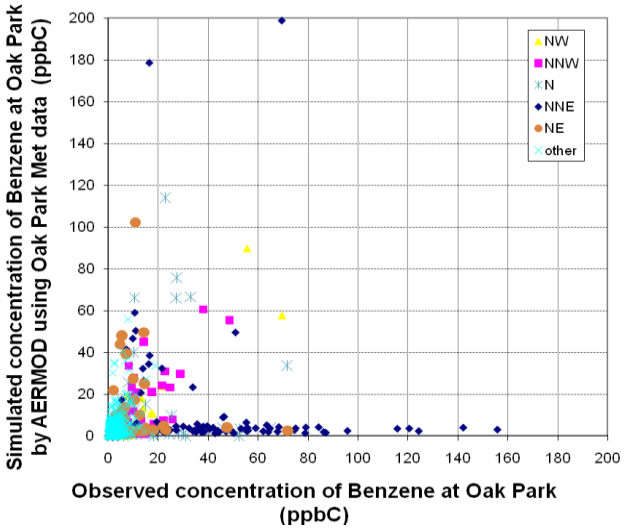

Figure 4.5 Scatter plot of predicted benzene concentrations from AERMOD (Oak Park met data) vs. observed concentrations at Oak Park

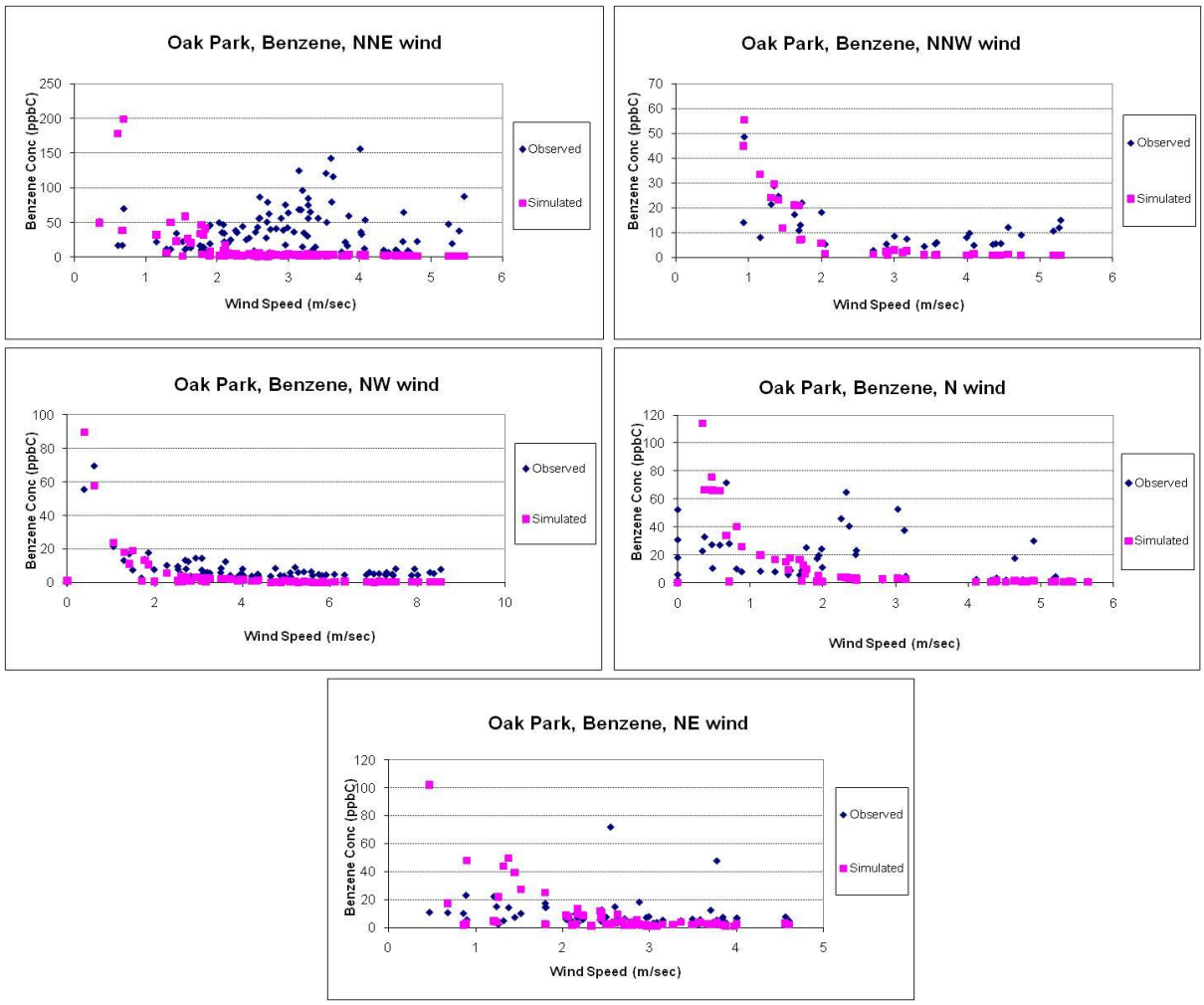

Figure 4.6 Benzene concentration's observation and AERMOD simulation against northern wind speed at Oak Park

Figure 4.7 shows the time of day of the maximum observed and predicted concentrations during the 2 month period. Observed maximum concentrations occur most frequently between 6 and 8 AM (CST), whereas predicted concentrations occur during the earlier hours (3~7 AM CST). Several days show maximum observed concentrations between the morning hours until noon, which are not captured by AERMOD. Otherwise, during the night when the atmospheric conditions are likely to be stable, there is reasonable agreement between observed and predicted hourly maximum concentration.

Figure 4.8 shows the time of day and number of hours of high benzene concentration (McGaughey et al. 2009, threshold concentration of 30 ppbC or over). Observational data and the AERMOD predicted concentration showed 69 and 42 hours each for the over 30 ppbC benzene concentration during the modeled period. AERMOD simulations were not able to predict the high benzene concentration during the 0800 CST till 1100 CST period. In Figure 4.9, daily maximum benzene concentration for the observed data at Oak Park and AERMOD simulated data are compared over the two-month period. Except for a couple of days, the daily maximum peak occurs during similar days of the month. The observed episode peaks occurred on November 3rd; the AERMOD predicted episode peaks occurred on November18th.

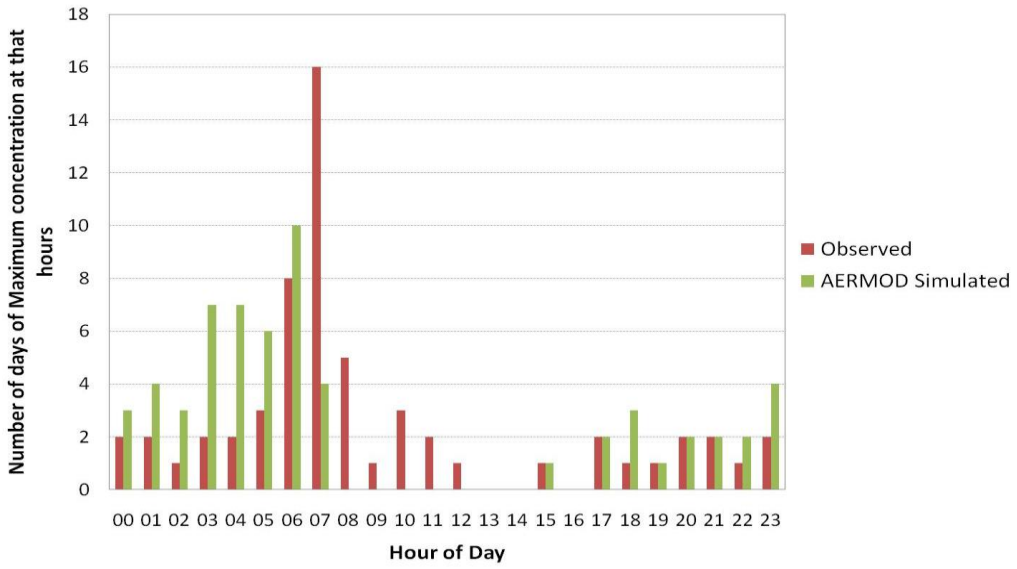

Figure 4.7 Time of day (hr) for maximum benzene concentration observed vs. simulated by AERMOD -during Oct-Nov 2006

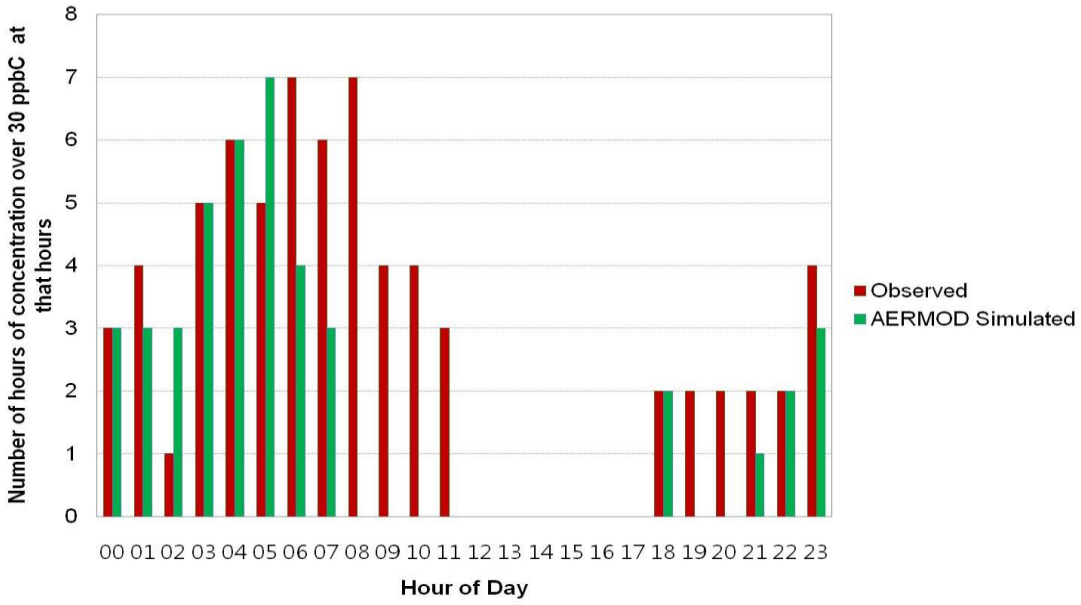

Figure 4.8 Time of day (hr) for benzene concentration observed vs. simulated by AERMOD with threshold over 30 ppbc -during Oct-Nov 2006

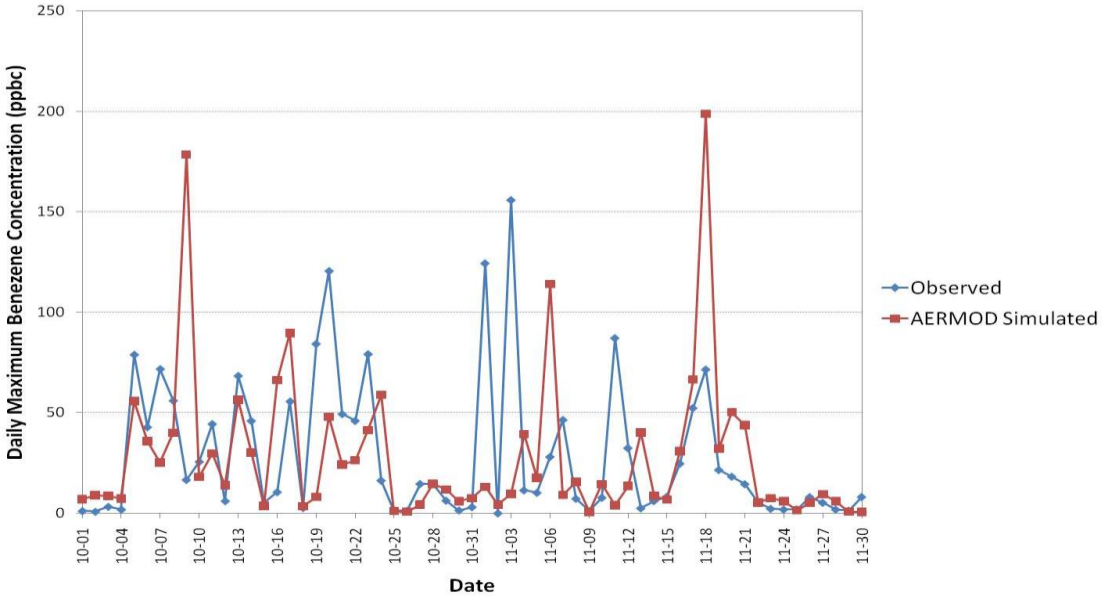

Figure 4.9 Comparison between observed and AERMOD simulation of daily maximum benzene concentration (ppbc) at Oak Park

A closer look at prevailing meteorological conditions on the unpaired maximum peak days (October 9th, November3rd, November 11th) was conducted using the Corpus Christi Trajectory Analysis Tool (http://www.utexas.edu/research/ceer/ccaqp/trajectory_tool.htm) as shown in Figure 4.10. On Oct 9th, the maximum observed concentration, 16.6 ppbC, occurred around 2 AM (CST), and AERMOD predicted concentration, 178.5 ppbC, at 3 AM (CST). Winds were calm during this period. In contrast, on November 3rd, the high concentration was observed, 155.8 ppbC, at 4 AM (CST) under very strong NNE winds. As shown above, elevated benzene concentrations observed during these strong NNE winds were not replicated by AERMOD, which only predicted 9.6 ppbC maximum on November 3rd, 9 PM (CST) and 2.9 ppbC at 4 AM (CST). For November 11th, the observed peak concentration, 87.2 ppbC, occurred around midnight. Wind direction and speed were fluctuating during this period which may have affected the large difference between the observed and modeled (AERMOD maximum prediction: 4 ppbC) maximum concentrations.

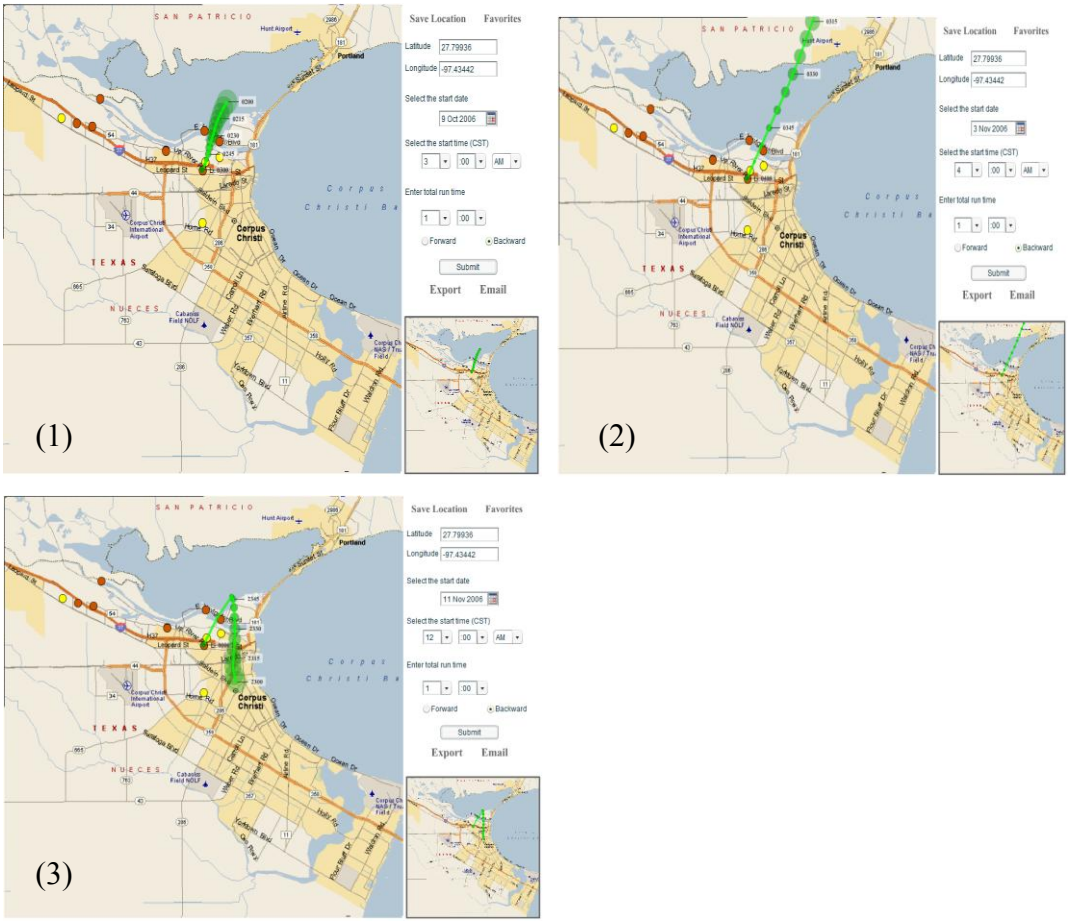

Figure 4.10 Back trajectory of wind using the Corpus Christi Trajectory Analysis Tool at (1) Oct. 9th, (2) Nov. 3rd, and (3) Nov. 11th

CALPUFF

CALMET, the preprocessor for meteorological data, was able to use data from 18 surface sites around the Corpus Christi area (including 7 monitoring sites operated by UT, and other NWS sites), 1 upper air site (Corpus Christi International Airport NWS site), 5 precipitation station sites and 1 buoy site. Figures 4.11 and 4.12 show the time series of observed benzene concentrations by wind direction and wind speed. Similar to AERMOD's result, northerly wind directions were, most frequently but not always,

associated with high elevated concentration of benzene. Under high wind speeds, predicted concentrations typically decreased at the site.

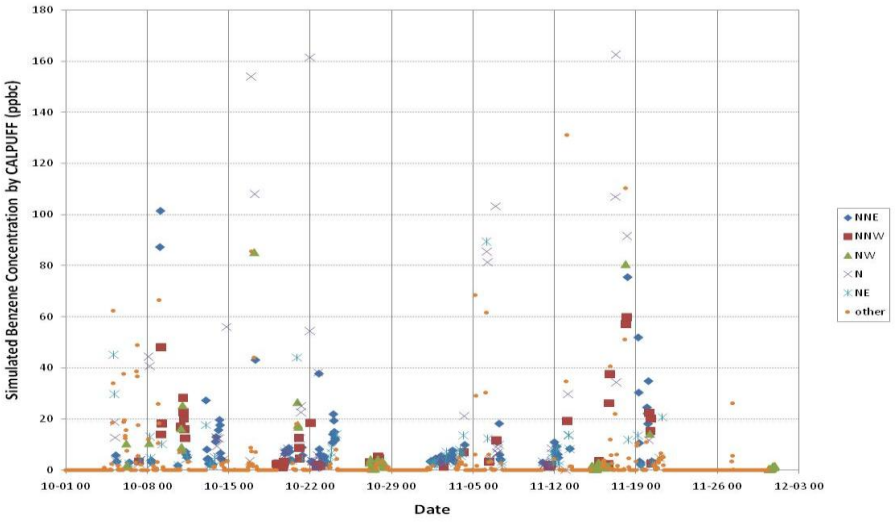

Figure 4.11 Time series of CALPUFF simulated benzene concentration at Oak Park by wind direction

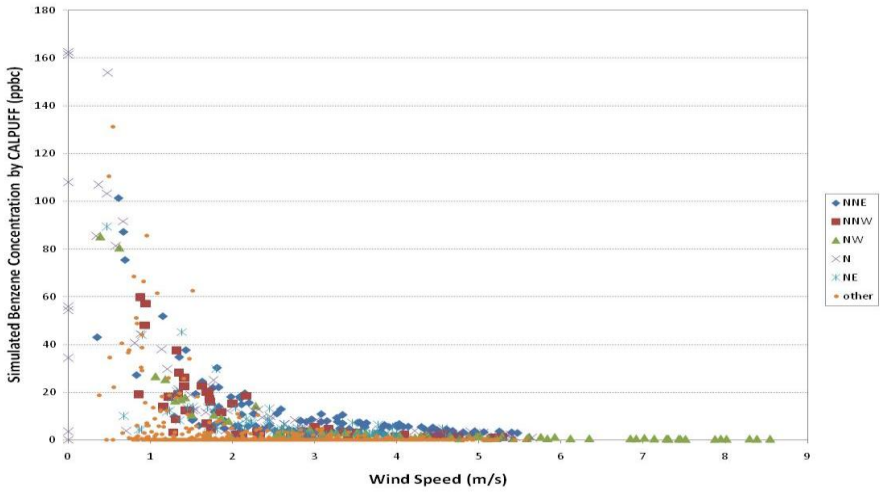

Figure 4.12 Relation to wind speed of simulated benzene concentration by CALPUFF at Oak Park

Figure 4.13 shows the scatter plot of the CALPUFF simulated benzene concentrations compared with observed concentrations binned by wind direction at the Oak Park site. Similar to AERMOD, CALPUFF could not simulate the high elevated concentrations observed during periods with stronger winds from the NNE direction. Other wind directions appear less biased toward underprediction. Comparisons between observations and CALPUFF predictions during northerly wind directions are shown in Figure 4.14.

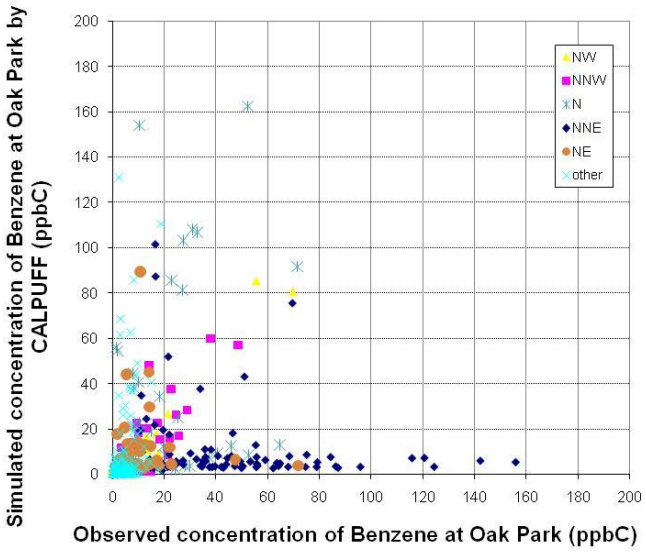

Figure 4.13 Benzene concentration scatter plot of CALPUFF simulation vs. observations at Oak Park

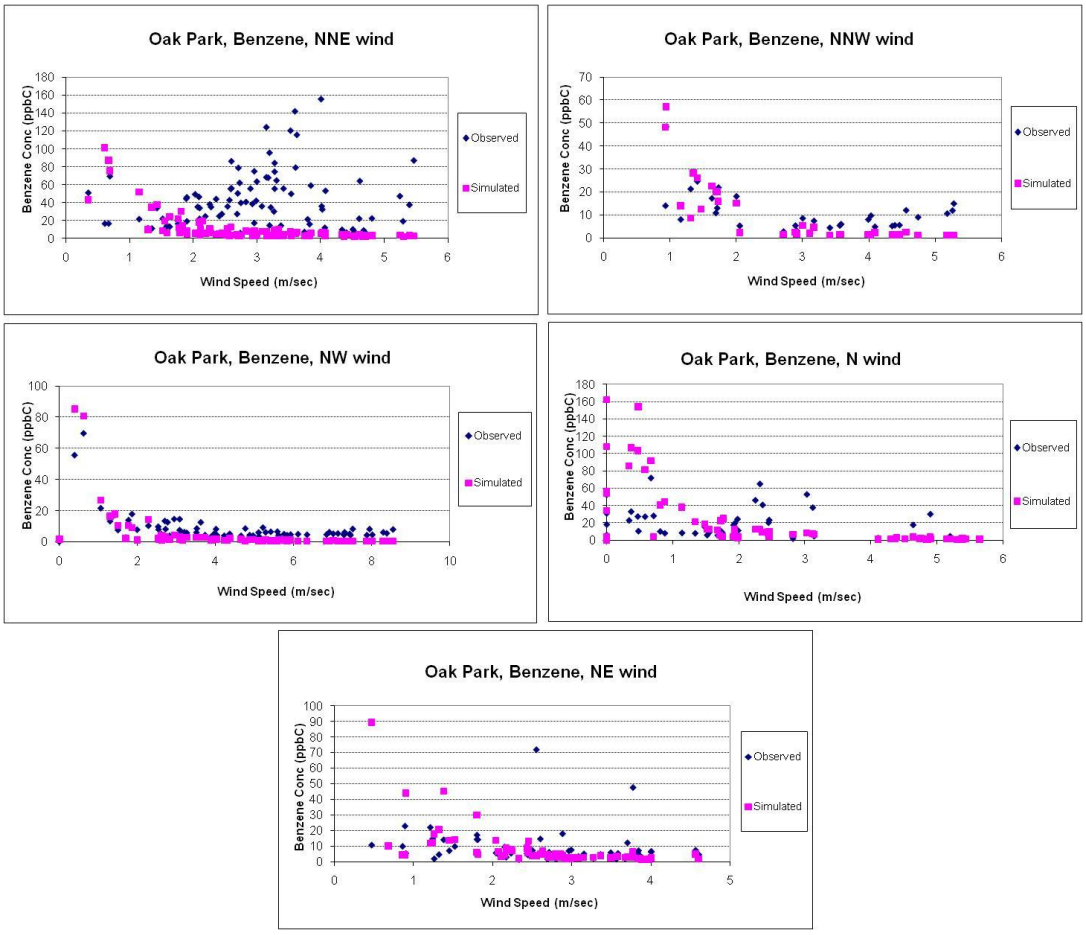

Figure 4.14 Observed benzene concentrations and CALPUFF simulations under northerly wind directions at Oak Park

Slightly different diurnal trends were evident for the time of day of the maximum CALPUFF predicted concentration than the AERMOD prediction. As shown in Figure 4.15, CALPUFF predicted the maximum concentrations to occur most frequently near midnight and the early morning periods. But for high benzene concentrations (McGaughey et al. 2009, threshold 30 ppbC), CALPUFF shows similar hourly trends with AERMOD predictions (Figure 4.16). CALPUFF predicted 49 hours of high benzene concentration during the October – November 2006 period, which is 7 hours more than

the AERMOD simulation, but still couldn't predict the observed high concentrations during the 0800 CST to 1100 CST morning period.

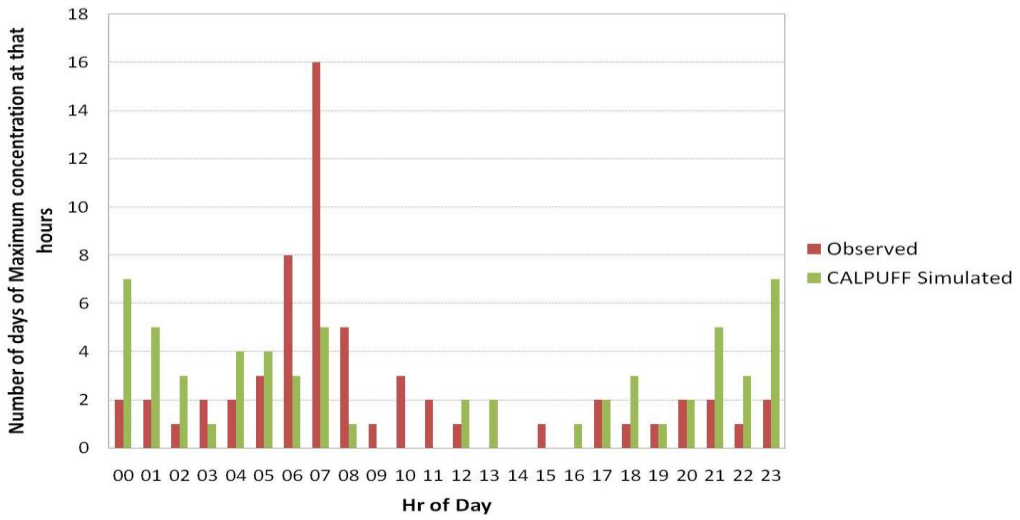

Figure 4.15 Time of day (hour) for observed and CALPUFF simulated maximum benzene concentrations during Oct-Nov 2006.

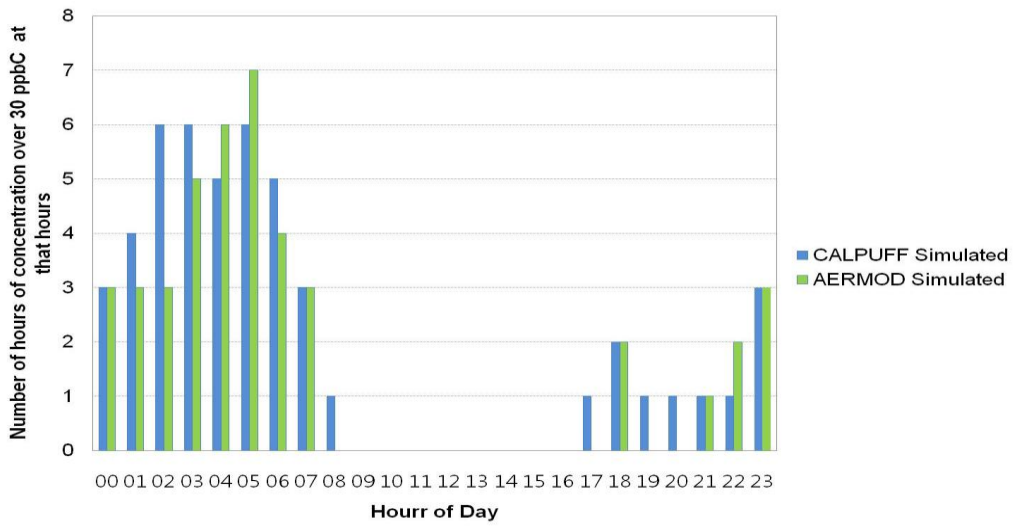

Figure 4.16 Time of day (hr) for benzene concentration over 30 ppbC simulated by AERMOD and CALPUFF

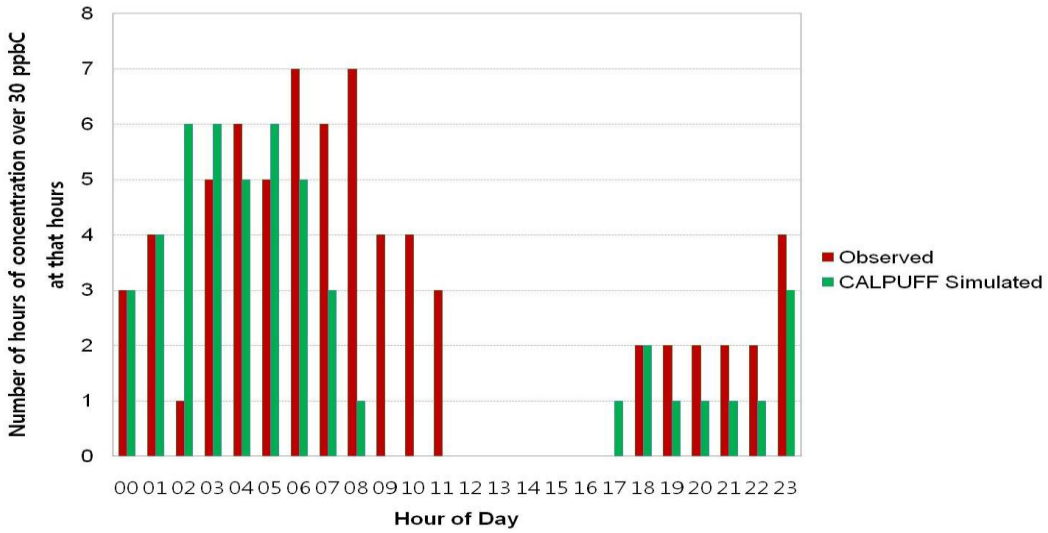

Figure 4.17 Time of day (hr) for benzene concentration observed vs. simulated by CALPUFF with threshold over 30 ppbc -during Oct-Nov 2006

Daily maximum observed and CALPUFF predicted benzene concentrations are compared in Figure 4.18. CALPUFF predicted slightly different behavior between October 20th and October 23rd, but the results were otherwise similar to AERMOD. Figure 4.19 compares the observed, AERMOD predicted, and CALPUFF predicted daily maximum concentrations.

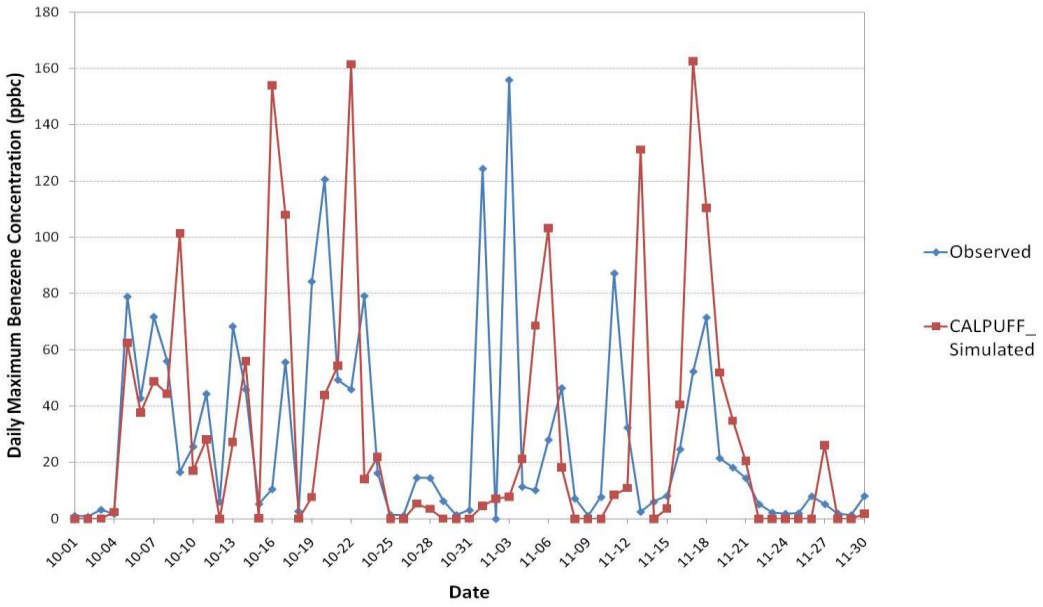

Figure 4.18 Comparison between observed and CALPUFF predicted daily maximum benzene concentrations (ppbc) at Oak Park

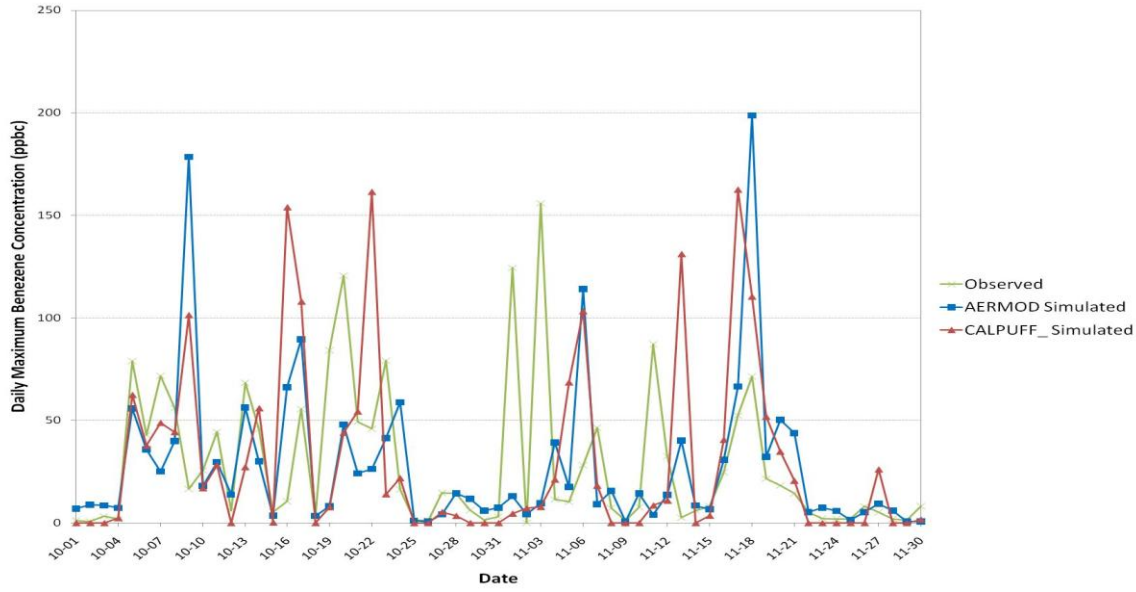

Figure 4.19 Comparison between observed, AERMOD and CALPUFF predicted daily maximum benzene concentrations (ppbc) at Oak Park

Model Inter-comparison

Scatter plots for AERMOD and CALPUFF predicted benzene concentration binned by wind direction are shown in Figure 4.20. CALPUFF predicts higher concentrations under non-northern winds with the wind speed under 1 m/sec (Figure 4.21). Overall, AERMOD and CALPUFF predictions for benzene concentrations for northern winds have better agreement than the non-northern winds. Table 4.1, shows the Mean Normalized Gross Error (MNGE) for the daily, weekly and monthly values:

$$MNGE = \frac{1}{N}\sum \frac{|P_i - O_i|}{O_i} \times 100\%$$

and Figure 4.22 shows the Mean Normalized Bias (MNB) for the two models within the same time periods as the MNGE (Tesche et al. 1991). P_i is the predicted value, and O_i stands for the observed value.

$$MNB = \frac{1}{N}\sum \frac{(P_i - O_i)}{O_i} \times 100\%$$

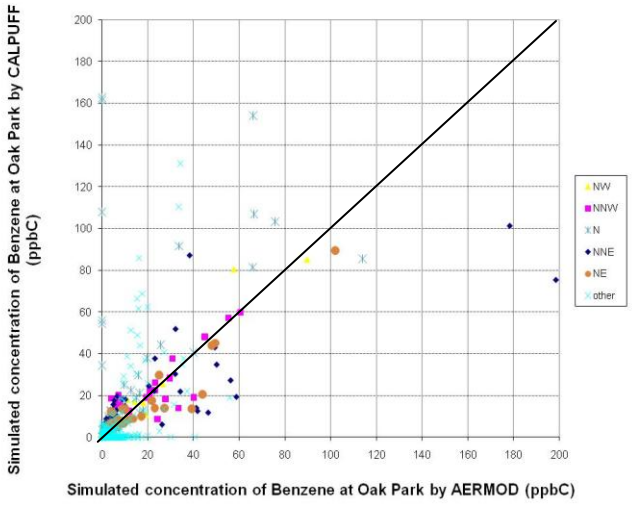

Figure 4.20 Benzene concentration scatter plot of AERMOD and CALPUFF simulation at Oak Park

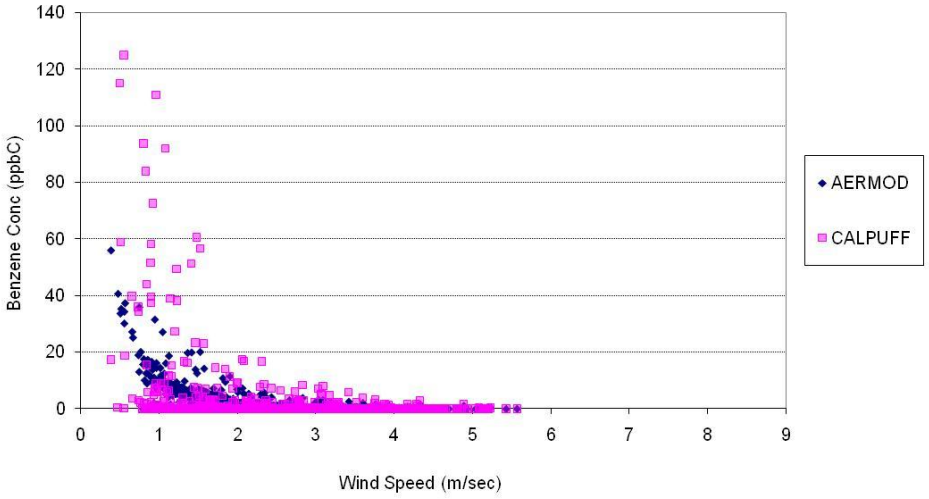

Figure 4.21 AERMOD and CALPUFF simulations under non-northerly wind directions at Oak Park

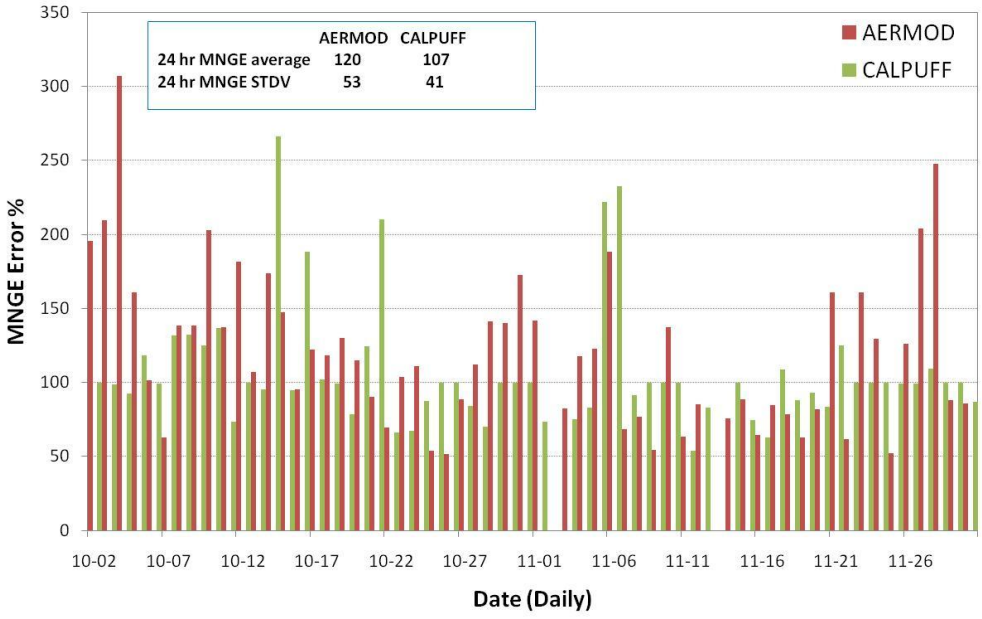

Figure 4.22 24 hr Mean Normalized Gross Error (%) for AERMOD and CALPUFF compared to observed benzene concentration data at Oak Park

Table 4.1 Weekly and monthly mean normalized gross Error (%) for AERMOD and CALPUFF compared to observed benzene concentrations at Oak Park

	AERMOD		CALPUFF	
DATE	Weekly MNGE (%)	Monthly MNGE (%)	Weekly MNGE (%)	Monthly MNGE (%)
Oct. 1st week	185.2		107.5	
Oct. 2nd week	154.1	135.4	132.9	111.8
Oct. 3rd week	116.4		128.5	
Oct. 4th week	86.5		81.1	
Oct. 5th - Nov. 1st week	132.5		88.7	
Nov. 2nd week	100.9		128.5	
Nov. 3rd week	98.0	110.7	134.3	111.9
Nov. 4th week	101.7		100.2	
Nov. 5th week	150.4		99.1	
Average	125.1	123.0	111.2	111.9
Standard Deviation	32.8	17.4	20.3	0.1

The predictions between AERMOD and CALPUFF are similar with respect to the MNGE, but CALPUFF's predictions shows 10% lower value than AERMOD. Tesche et al. (1991) proposed a goal of MNGE to be within in 35% for ozone regulatory modeling. From this point of view, both AERMOD and CALPUFF predictions for benzene concentration at Corpus Christi during the 2 month modeling period was a factor of 3.6 greater than the desired performance.

Figure 4.23 and Table 4.2 show the Mean Normalized Bias (MNB) for daily, weekly, and monthly periods. The MNB for AERMOD exhibits changes within approximately two-week periods, whereas CALPUFF shows a stronger negative bias relative to observed values. Longer-term modeling would be beneficial to evaluate the performance of the models.

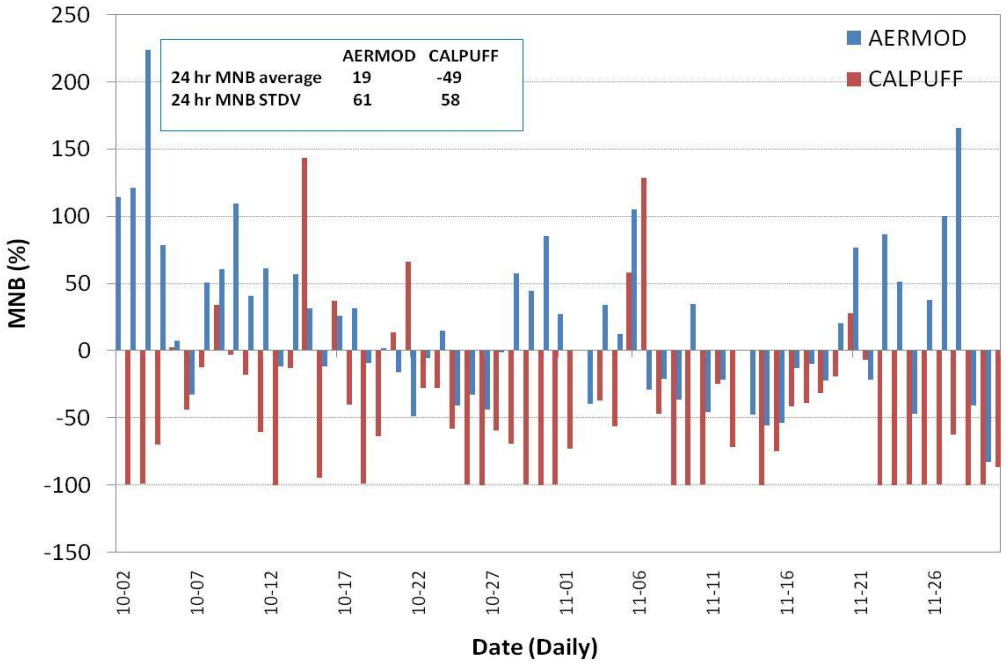

Figure 4.23 24 hr. Mean Normalized Bias (%) for AERMOD and CALPUFF compared to observed benzene concentration data at Oak Park

Table 4.2 Weekly and monthly mean normalized bias (%) for AERMOD and CALPUFF compared to observed benzene concentrations at Oak Park

	AERMOD		CALPUFF	
DATE	**Weekly MNB (%)**	**Monthly MNB (%)**	**Weekly MNB (%)**	**Monthly MNB (%)**
Oct. 1st week	98.9		-49.4	
Oct. 2nd week	52.4	34.6	-2.1	-40.1
Oct. 3rd week	7.3		-24.8	
Oct. 4th week	-21.9		-61.1	
Oct. 5th - Nov. 1st week	34.9		-77.7	
Nov. 2nd week	2.1		-25.4	
Nov. 3rd week	-13.0	10.2	-8.5	-44.5
Nov. 4th week	20.9		-57.1	
Nov. 5th week	36.0		-89.5	
Average	24.2	22.4	-44.0	-42.3
Standard Deviation	36.9	17.3	30.5	3.1

Discussion

Observed benzene concentrations at Oak Park do not indicate significant differences between weekday and weekend activities. In Figure 4.7, hourly maximum concentrations are mostly observed during the early morning hours, which may originate from industrial or mobile sources or port activities or may be due to meteorological conditions. Morning hour benzene concentration peaks are consistent with McCarthy et al.'s (2007) nationwide study within the U.S. High benzene concentration over 30 ppbC were likely to be observed mostly within northern wind direction (Figure 4.1, 4.2), which is not a surprise since the Oak Park monitoring station is south of the major emission sources including industrial emissions and possible mobile emissions due to the roadway, Interstate-37. Low performance of the two models unable to predict high benzene concentration in the morning hours (0800 CST till 1100 CST, Figure 4.8 and Figure 4.16) could be an evidence of need for other emission sources such as mobile source emissions (only point sources are modeled in this work). Stronger winds from the NNE direction were associated with elevated benzene concentrations at Oak Park. AERMOD and CALPUFF could not replicate the elevated concentrations under strong NNE winds. The timing of AERMOD predicted hourly maximum concentrations and daily maximum concentrations generally showed reasonable agreement with observations. The daily maximum peaks which AERMOD couldn't predict, CALPUFF couldn't predict either. Considering the dates for high benzene concentration (30 ppbC and over, McGaughey et al. 2009) from the daily maximum concentrations from observation data, AERMOD predicted the closest (minimum for 'observation value – predicted value') on October 6th, and CALPUFF predicted best on October 21st (Figure 4.19). The largest gap (maximum value for 'observation value – predicted value') was on November 3rd for both models (Figure 4.19). Overall, the best agreement between models and observations for both

AERMOD and CALPUFF was October 6th, and the worst prediction was on November 3rd.

Three major peaks were observed in the Oak Park time series of observed concentrations under different conditions. AERMOD and CALPUFF couldn't replicate the maximum peak observed on November 3rd, 2006, which was detected during relative strong winds (4 m/s) from the NNE direction (Figure 4.6, 4.14). Simulating benzene concentrations during stronger wind conditions and unstable meteorology should be further investigated. Both AERMOD and CALPUFF had a Mean Normalized Gross Error average of approximately 107~120%. Table 4.3 is a summary of the highest daily maximum hourly concentrations for each dataset during the October-November 2006 period. AERMOD exhibited the highest predicted concentration of 198.7 ppbc on Nov. 18th, when the observation data from Oak Park monitoring station was 71.5 ppbc. CALPUFF predicted the maximum concentration on Nov. 17th, which over predicted the observation concentration, 52.4 ppbC. Dates of the highest benzene concentration between Oak Park monitored data, AERMOD and CALPUFF were not necessarily coincident. Longer-term modeling would be useful to further assess the model predictions

Table 4.3 Maximum benzene concentrations at Oak Park during Oct –Nov.2006 (observed and predicted)

	Observed	date	AERMOD	date	CALPUFF	date
Maximum Concentration(ppbc) and date	155.8	Nov. 3	198.7	Nov. 18	162.5	Nov. 17
Observed Concentration (ppbc)		difference *	71.5	127	52.4	110
AERMOD Predicted (ppbc)	9.6	-146		difference*	66.5	14
CALPUFF Predicted (ppbc)	7.9	-148	110.4	39		difference*

* difference = predicted - observed

5 SPATIAL AND SENSITIVITY STUDIES

Sensitivity to meteorological data input for AERMOD

AERMOD uses a single set of meteorological data, which makes the prediction highly sensitive to the choice of meteorological data input (Paine et al. 2003). In the results described in the previous chapter, the Oak Park on-site meteorological data was used for the AERMOD simulation. These predictions could not match the high benzene concentrations observed on Nov. 1st and 3rd and 11th (Figure 4.9). To verify if these discrepancies could be due to the choice of meteorological data, three different sets of meteorological data from different CCNAT monitoring sites (Solar estates, Port Grain, J.I. Hailey) were used with AERMOD. Figure 5.1 shows the daily maximum benzene concentrations during the Oct – Nov. 2006 period using these meteorological data. The Port Grain monitoring site and the J.I. Hailey monitoring site are near to each other (Table 2.1, Figure 2.2, 2.3) which results in similar peak patterns. AERMOD results using the Solar Estates monitoring site's, which is the farthest CCNAT monitoring site from the Oak Park monitoring site, had the lowest predicted maximum concentration. None of these meteorological data were able to predict the high observed concentration mentioned above, and all had a negative bias relative to the observed values (Figure 5.2).

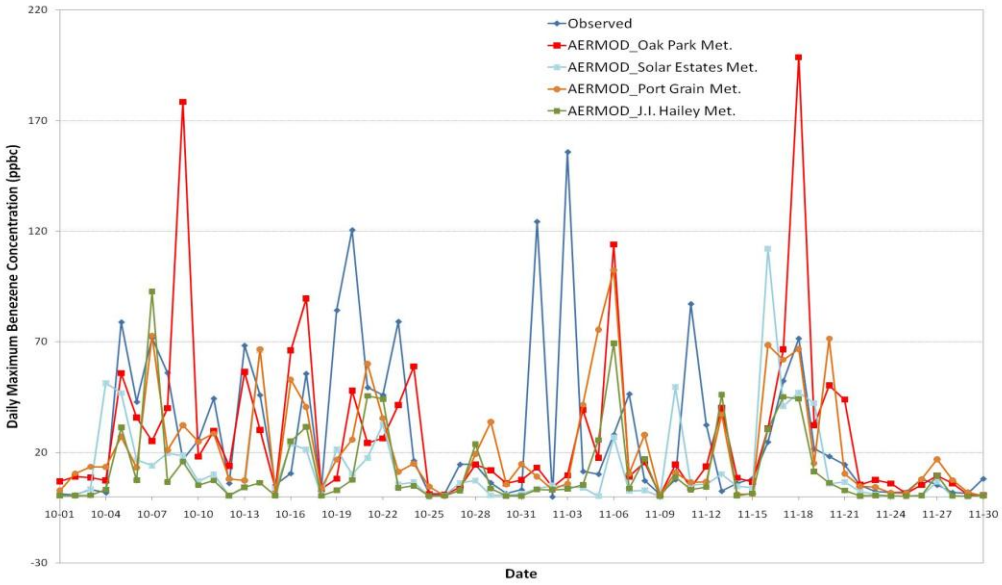

Figure 5.1 Comparison between observed and AERMOD simulation of daily maximum benzene concentration (ppbc) at Oak Park with different meteorological input

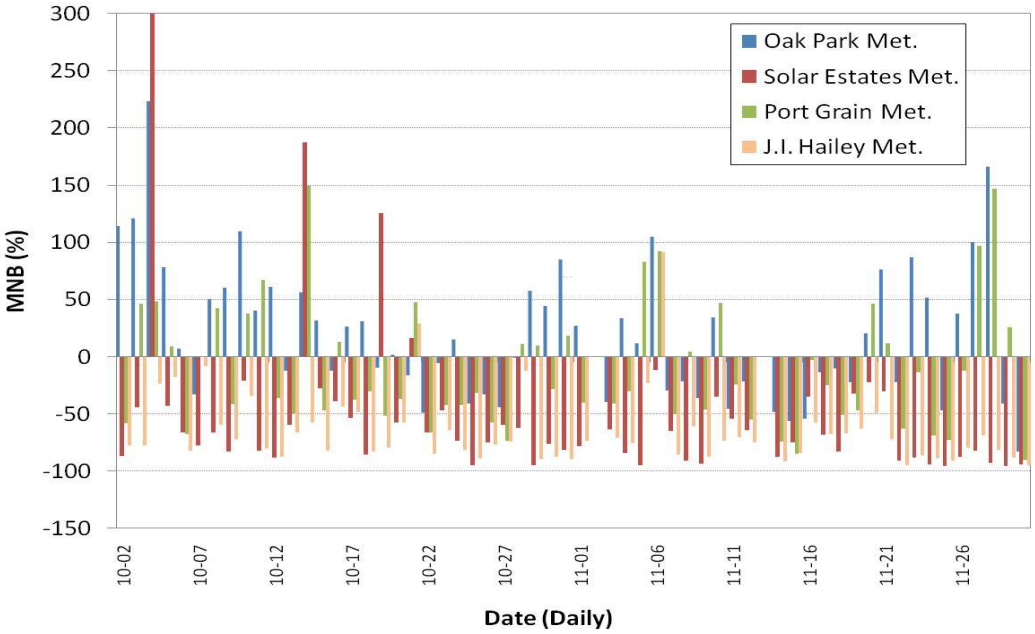

Figure 5.2 24 hr. Mean Normalized Bias (%) for AERMOD, using different meteorological data set, compared to observed benzene concentration data at Oak Park

Spatial sensitivity

The results shown in Figure 5.1 indicate that, although there is a negative bias in the AERMOD predictions, on some days the predictions based on the Oak Park meteorology lead to overpredictions. This suggests that concentration magnitudes may be correctly predicted, but that plume tracks are not being precisely predicted. To examine this possibility, receptor miss-location in AERMOD was considered. The Oak Park monitoring site locations was placed in the middle of a grid of point receptors, separated by a distance of 500m that formed a 1 x 1 km square (Figure 5.3). Figure 5.4 shows the predicted daily maximum benzene concentrations for this grid of receptors. The three points located north to the Oak Park site predict higher concentration on Nov. 1st than the Oak Park site, and the north east corner receptor (+0.5km, +0.5km) shows the highest concentration. But as seen in Figure 5.3, these three receptors are much closer to the industrial source region. The highest benzene concentration observed on Nov 3rd was larger than the predicted concentration at all receptor points.

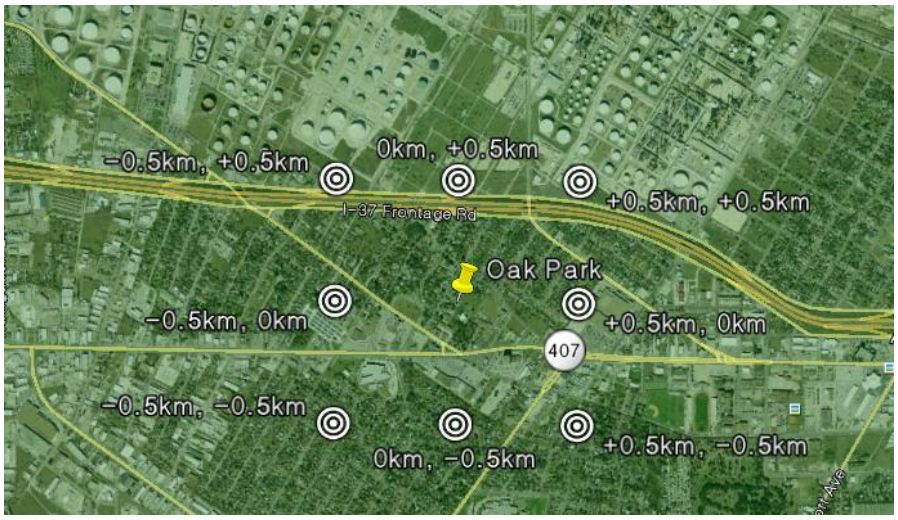

Figure 5.3 AERMOD receptor point analysis for ±500m distance from the Oak Park monitoring site

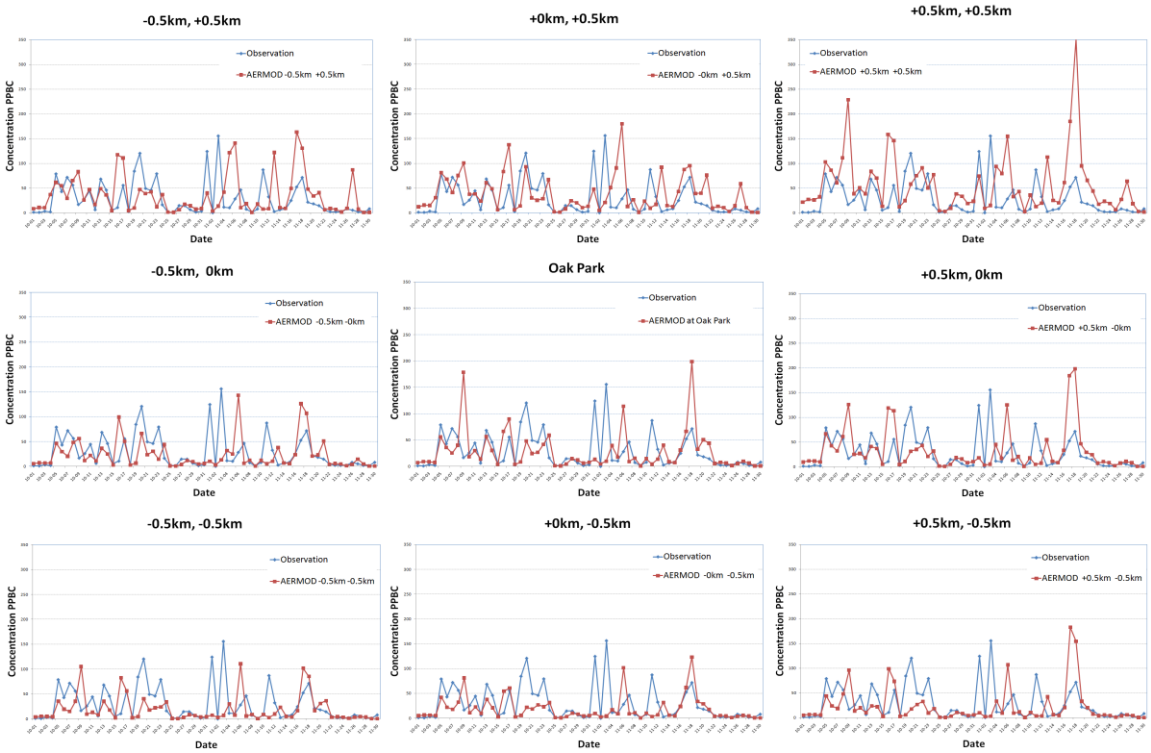

Figure 5.4 Comparison between observed and AERMOD predicted daily maximum benzene concentrations (ppbc) at Oak Park for point receptors around

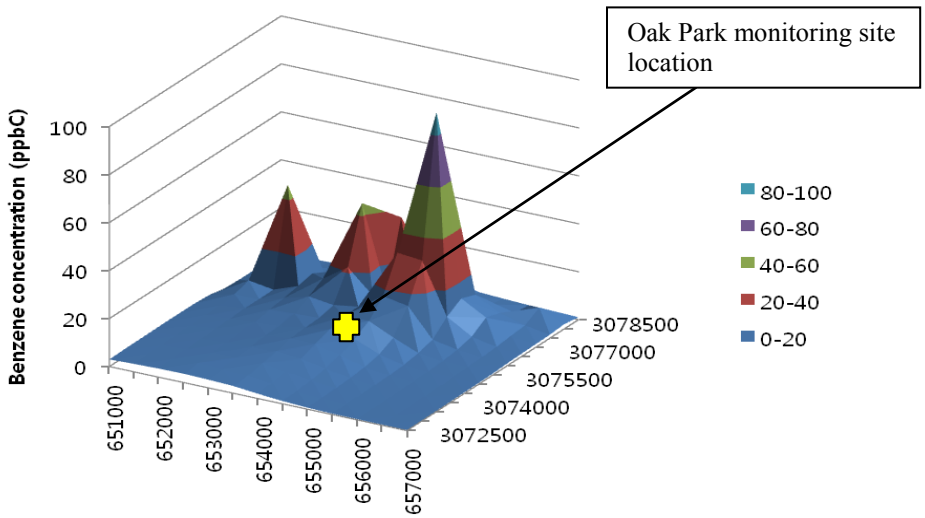

Figure 5.5 Surface plot of AERMOD simulated benzene concentration near the Oak Park site on Nov. 3rd (UTM coordinate)

Similar evaluation using CALPUFF on the data from Nov 3rd was performed. Using the PAVE (http://paved.sourceforge.net/) tile plot (Figure 5.6), we were able to see the concentration gradient degradation from the emission source from the North-east direction, but still, no estimates of high benzene concentration are shown near the Oak Park monitoring site. Note that Figure 5.6 is in Lambert Conformal Conic projection (LCC) coordinates and the concentration is in ppb.

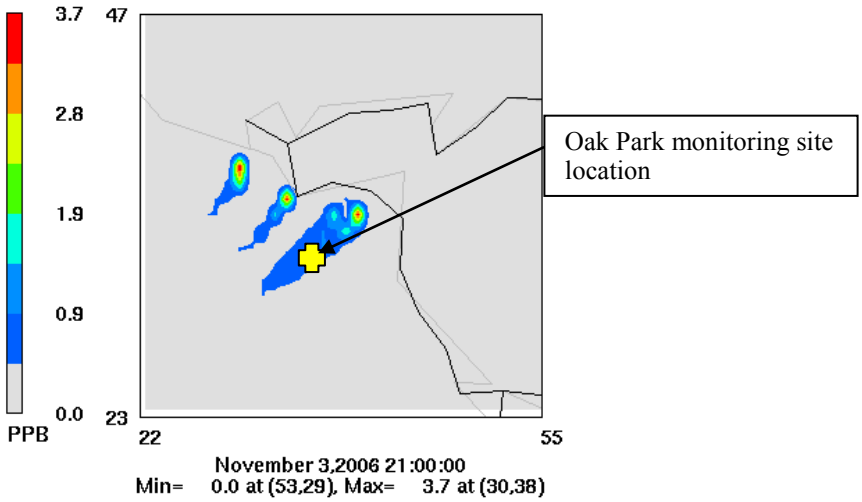

Figure 5.6 PAVE tile plot of CALPUFF predicted benzene concentration on Nov. 3rd

Terrain height sensitivity

The Oak Park monitoring station's elevation value used in the AERMOD simulations was 10.78 meters calculated from the digital elevation model (DEM) files used with AERMAP. To verify possibilities of elevation height sensitivities which might cause the differences between observed and predicted benzene concentrations, AERMOD benzene predictions were estimates for two different heights than the original 10.78 meters. 1 meters, and 20.78 meters height were chosen for the heights for the Oak Park monitoring site. Figures 5.7 and 5.8 show the scatter plots of the simulated concentration

of benzene at Oak Park with different elevation height values compared to the observed data at Oak Park binned by wind direction, and the concentrations plotted for the NNE wind speed. Compared to the original height data, no significant difference was observed (Figure 5.9)

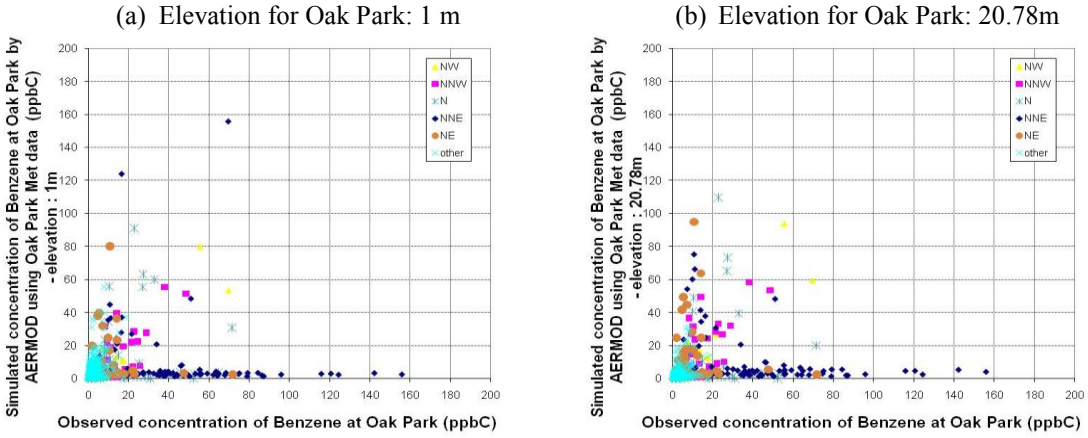

Figure 5.7 Scatter plot of predicted benzene concentrations from AERMOD (with different elevation at Oak Park) vs. observed concentrations at Oak Park

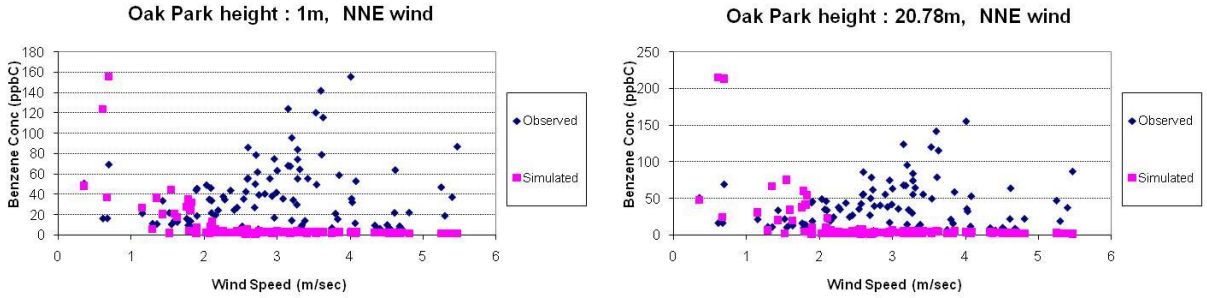

Figure 5.8 Benzene concentration's observation and AERMOD simulation against NNE wind speed at Oak Park for different Oak Park site elevation

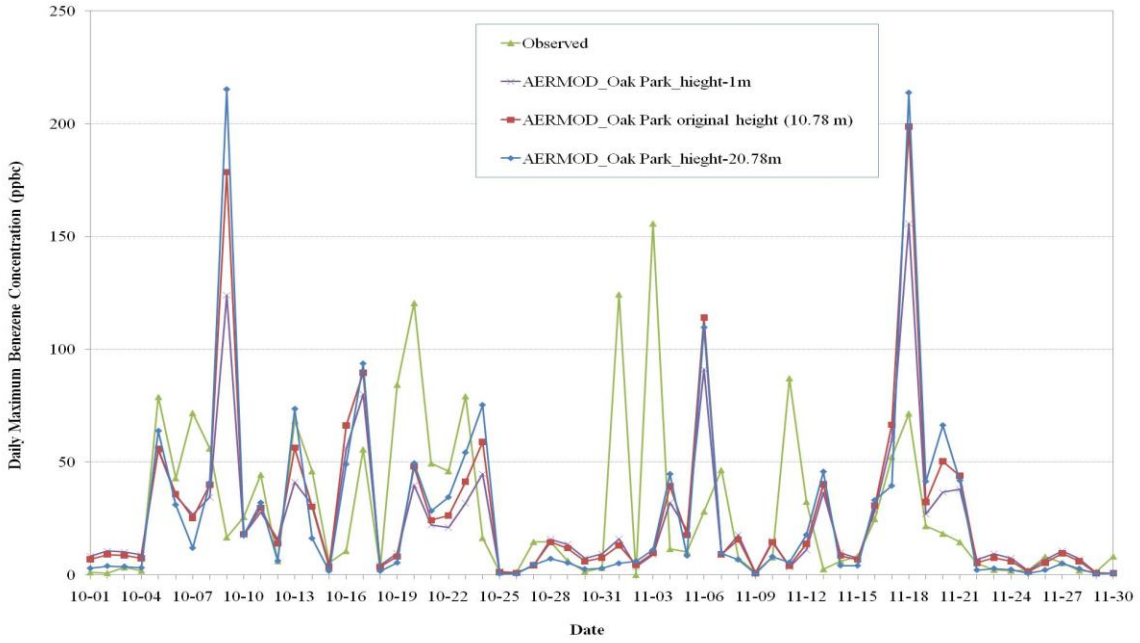

Figure 5.9 Comparison between observed and AERMOD simulation of daily maximum benzene concentration (ppbc) at Oak Park for different elevations

Stack-tip downwash effect

Since the differences between the observed and predicted benzene concentrations are largest for strong NNE wind conditions, stack-tip downwash for industrial sources may be important. Wind flowing past a stack can cause a region of decreased pressure to form downwind (Turner et al. 2007). This might cause the high observed concentrations for strong NNE wind conditions at Oak Park. But AERMOD's default calculation already embeds this stack-tip downwash algorithm, so a non-default option for suppressing the use of stack-tip downwash calculation (NOSTD) was used to verify its effect at the Oak Park site. From Figure 5.10 and 5.11, with the stack-tip downwash off, AERMOD prediction is only slightly lower than the default (stack-tip downwash on) calculation

which indicated that the model evaluates this as a modest effect. This was also true for varied Oak Park site elevations (Figure 5.12, November 3rd data.)

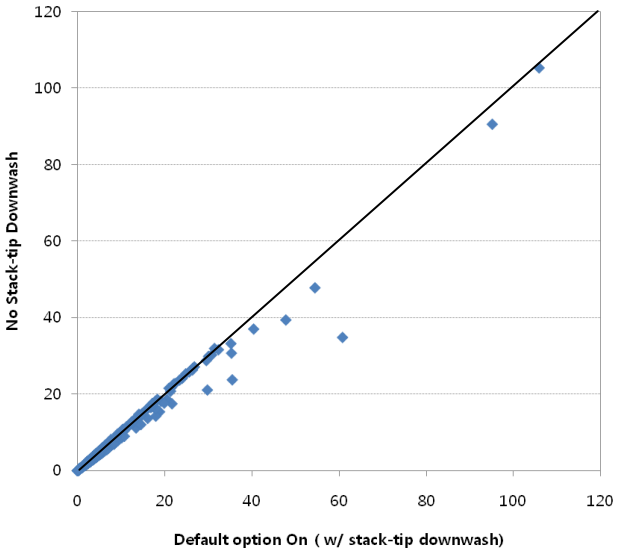

Figure 5.10 Scatter plot of predicted benzene concentrations (µg/m^3) from AERMOD with different stack-tip down wash calculation on/off at Oak Park

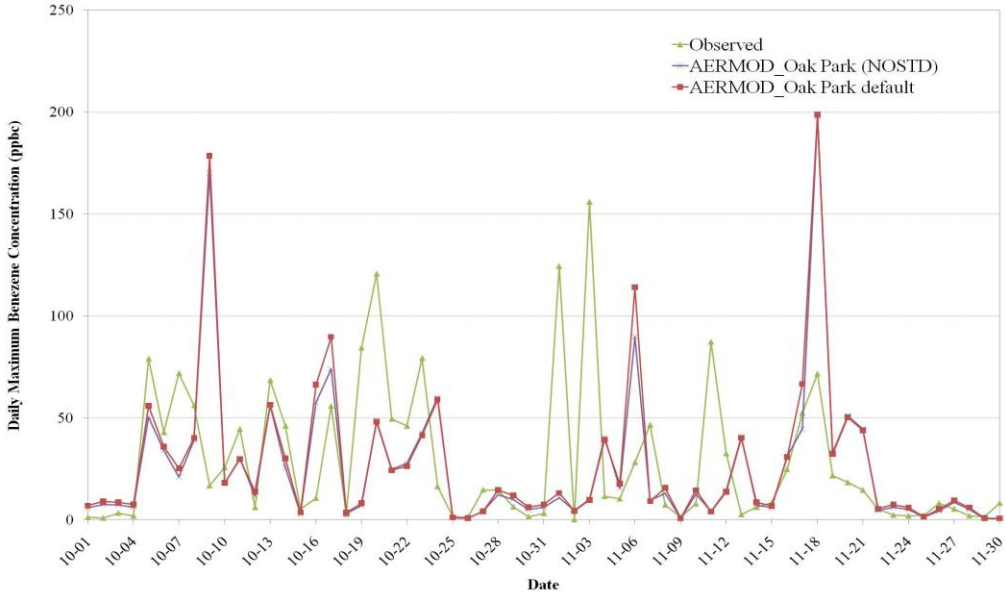

Figure 5.11 Comparison between observed and AERMOD simulation of daily maximum benzene concentration (ppbc) at Oak Park for stack-tip downwash option on and off (NOSTD)

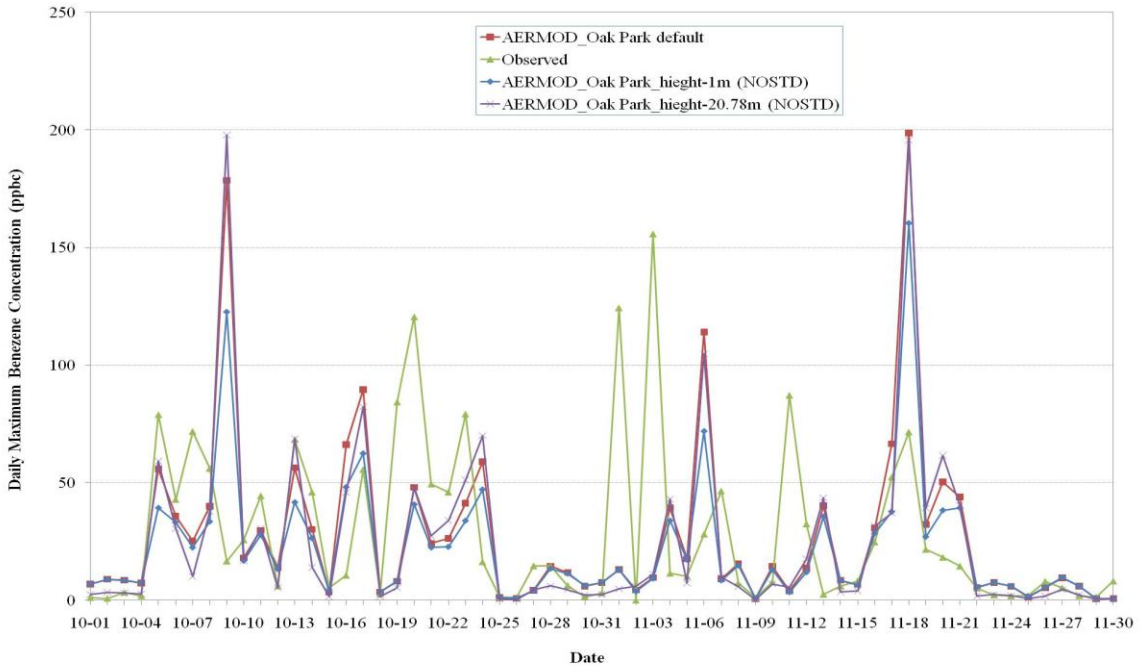

Figure 5.12 Comparison between observed and AERMOD simulation of daily maximum benzene concentration (ppbc) at Oak Park for stack-tip downwash option on and off (NOSTD) for different elevations

Emission inputs

Emission inputs could also lead to model inaccuracies. This is a difficult issue to address, since there are no independent, direct measurements of emissions. To investigate whether emission inaccuracies might be playing a role in benzene underpredictions, the concentrations of a second compound, propane, were modeled. Propane was chosen because it originates in very different parts of refining operations than benzene, so it is likely that under- and over-predictions of propane and benzene would not be correlated if the cause were emissions errors. In contrast, it over- and under-predictions were due to inaccurate dispersion modeling, the differences for the two compounds should be correlated. With propane emissions from the 2005 TCEQ Photochemical Modeling

Inventory (McDonald-Buller et al. 2009), AERMOD was used to predict the propane concentration at the Oak Park site.

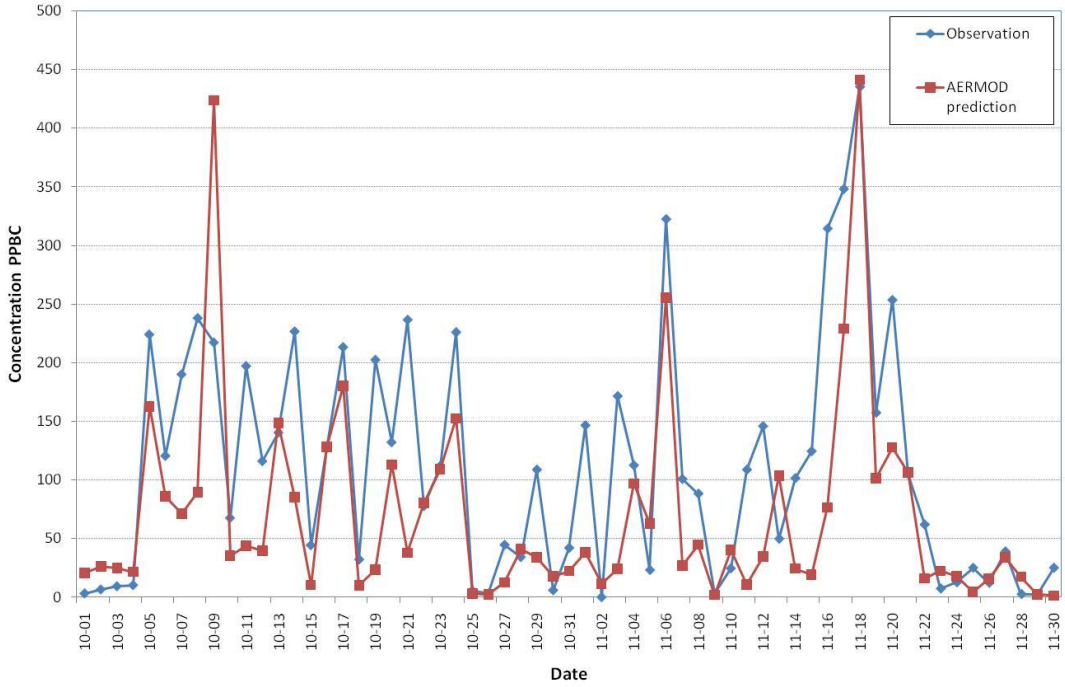

Figure 5.13 Comparison between observed and AERMOD predicted daily maximum propane concentrations (ppbc) at Oak Park

Figure 5.13 compares the daily maximum propane concentration observation at the Oak Park site and the AERMOD predicted value. High propane concentrations are observed and simulated on similar dates as with benzene (Figure 4.18). Figure 5.14 indicates the similar tendency for the 24 hour Mean Normalized Gross Error (MNGE) for the two pollutants.

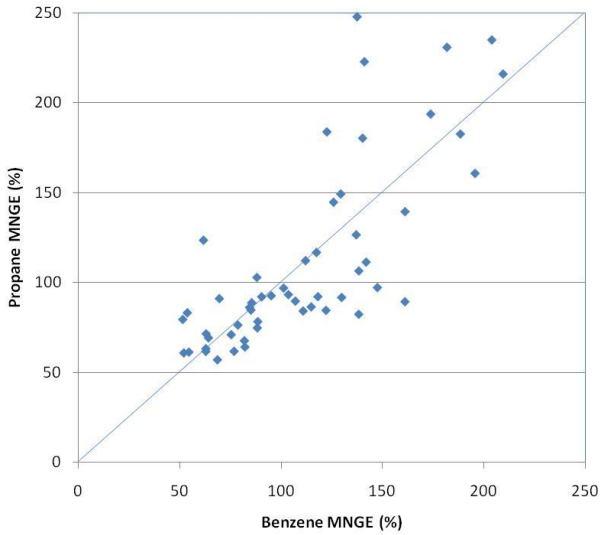

Figure 5.14 Scatter plot for 24 hr Mean Normalized Gross Error (%) for benzene and propane predicted value by AERMOD at the Oak Park site

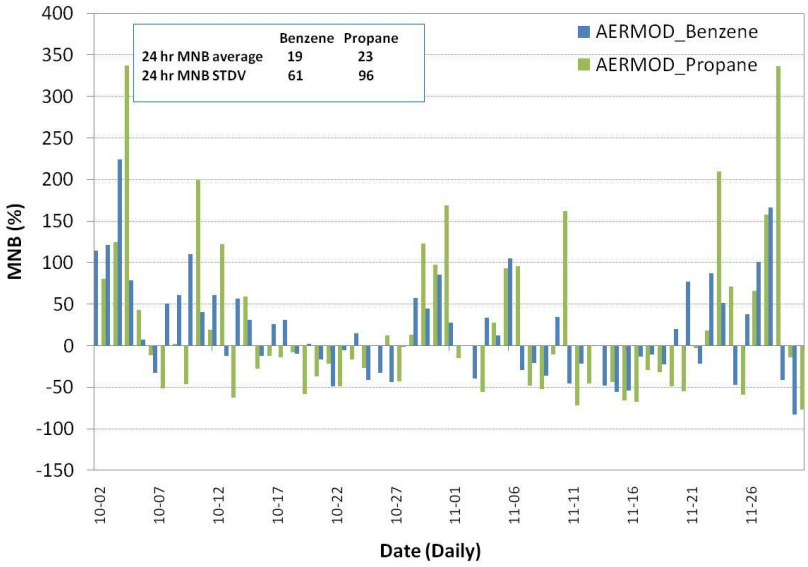

Figure 5.15 24 hr. Mean Normalized Bias (%) for AERMOD predicted benzene and propane concentrations compared to observed concentration data at Oak Park

The Mean Normalized Bias (MNB) for propane is also consistent with the benzene results (Figure 5.15). The MNB for propane exhibits changes within approximately two-week period, the same as the benzene's MNB. This suggests that emission inventories inaccuracies are likely not the dominant cause of the differences between predicted and observed values.

New version of AERMOD comparison

During the study, a modified version of AERMOD (ver.09292) was released by EPA. Modifications including subroutines for the dry/wet deposition calculations were in the version change (full descriptions are available at EPA web site: (http://www.epa.gov/scram001/dispersion_prefrec.htm). To ensure that the new model modification for AERMOD version 09292 doesn't affect the previous version's (ver. 06341) conclusions, benzene concentrations was simulated and compared between the previous and new version of AERMOD (Figure 5.16). Regardless of the version of AERMOD, the results were consistent.

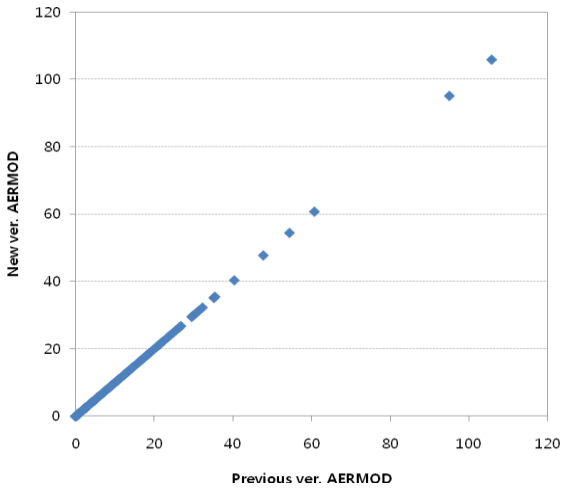

Figure 5.16 Scatter plots of predicted benzene concentrations (μg/m^3) from AERMOD between previous version (06341) and the new version (09292) at Oak Park

Sensitive receptors analysis

The concentrations of benzene at one hundred and forty one sensitive receptors (e.g. schools, hospitals, clinics, population center, and universities) around Corpus Christi area were predicted using AERMOD and CALPUFF during the 2 month period (Oct – Nov. 2006). Population centers were selected from the 2000 CENSUS data, schools from the Texas Education Agency (http://ritter.tea.state.tx.us) and the Texas General Land Office web site (http://www.glo.state.tx.us). Other receptors were also selected from the Texas General Land Office web site. Figure 5.17 indicates the locations of these receptors and the emission points with benzene extracted from the 2005 TCEQ Photochemical Modeling Inventory (McDonald-Buller et al. 2009). High benzene hours were defined as those hours characterized by a benzene concentration of 30 ppbC or greater. The threshold concentration of 30 ppbC is well below the short-term concentration values determined by TCEQ's Effects Screening Levels (ESLs), but above the long term value. ESLs are screening levels used in TCEQ's air permitting process in order to evaluate air dispersion modeling's predicted impact (http://www.tceq.state.tx.us/implementation/tox/esl/ESLMain.html). ESLs are based on potential for health effects, odor nuisances, vegetation effects, or corrosive effects. Adverse health or welfare effects are not expected to occur if the air concentration of a constituent is below its ESL. If an air concentration of a constituent is above the screening level, it is not necessarily indicative that an adverse effect will occur, but rather that further evaluation is warranted. The corresponding short-term (1 hour averaging) and long-term (annual averaging) ESLs for benzene are 324 ppbC and 8.4 ppbC, respectively. The latest ESL list is available at http://www.tceq.state.tx.us/implementation/ tox/esl/list_main.html#esl_1.

In Table 5.1, daily 1-hour maximum benzene concentration predicting over 30 ppbC (either AERMOD of CALPUFF, or for both) for the discrete receptors are listed,

including the total hours of predicted high benzene concentration (over 30ppbC) for the corresponding receptor. Though the date of maximum benzene concentration prediction between the two models were different, and some of AERMOD's predicted locations were not simulated with CALPUFF, most of the hot spots for potential high benzene concentration locations were consistent for the two models.

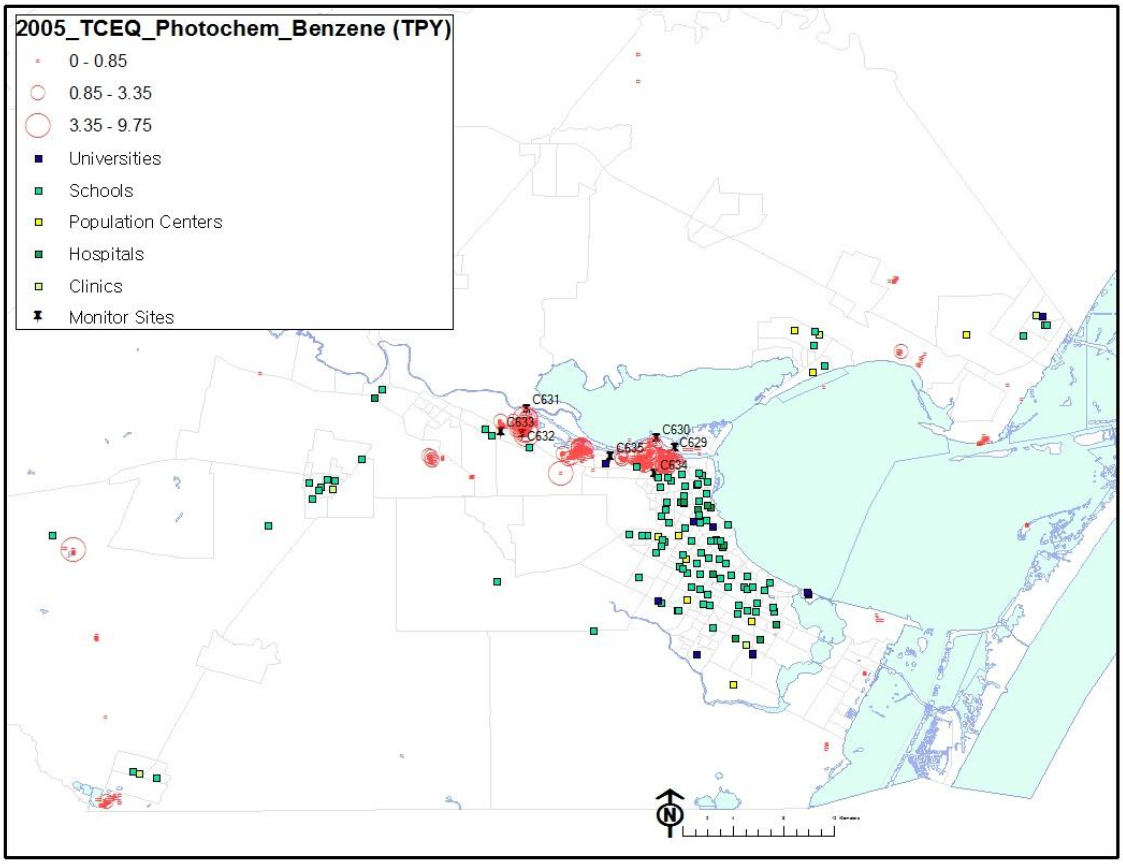

Figure 5.17 Location of discrete receptors and benzene emission points from 2005 TCEQ Photochemical Modeling Inventory

Figure 5.18 indicates the receptors predicting high benzene concentrations (over 30 ppbC) scaled by the benzene concentration in ppbC, and Figure 5.19 similarly shows the same receptors scaled by the hours of predicting for high benzene concentration. It is

not a surprise that for receptors near emission sources, higher benzene concentrations for more hours are predicted. Although the receptors with the highest and most frequent high benzene concentration predicted are likely to be near the emission sources (receptor numbers 20, 23, 65, 70, 75, 80, 88, etc), there were some predicted hot spots (not as high and frequent as the near source receptors) simulating high benzene concentrations such as receptor numbers 114, or 51, 56, and 95 for a value of 31~35 ppbC for a distance (2~7 km) away from the emissions. (The receptor numbers are given only for identification and have no other significance)

Table 5.1 Summary of discrete receptors' AERMOD/CALPUFF predicted maximum benzene concentration over 30 ppbC (from either or both models) and date of occurrence, including number of hours predicted over 30 ppbC during Oct – Nov. 2006

	Population Centers		AERMOD			CALPUFF		
receptor #	Lat	Long	Max. Conc. (PPBC)	Date of Occurrence mm-dd-hh	# of hours over 30 ppbC	Max. Conc. (PPBC)	Date of Occurrence mm-dd-hh	# of hours over 30 ppbC
2	27.765	-97.424	102.5	11-06 05	5	28.8	10-17 06	0
3	27.755	-97.432	67.1	11-17 06	4	23.4	10-17 06	0
4	27.756	-97.417	58.5	11-06 05	2	23.7	10-17 06	0
5	27.739	-97.412	31.1	11-06 05	1	17.2	10-17 06	0

	Clinics		AERMOD			CALPUFF		
receptor #	Lat	Long	Max. Conc. (PPBC)	Date of Occurrence mm-dd-hh	# of hours over 30 ppbC	Max. Conc. (PPBC)	Date of Occurrence mm-dd-hh	# of hours over 30 ppbC
15	27.77908	-97.41338	50.0	11-18 04	5	46.8	10-17 06	3

	Schools		AERMOD			CALPUFF		
receptor #	Lat	Long	Max. Conc. (PPBC)	Date of Occurrence mm-dd-hh	# of hours over 30 ppbC	Max. Conc. (PPBC)	Date of Occurrence mm-dd-hh	# of hours over 30 ppbC
20	27.77972	-97.42528	135.6	11-06 05	7	57.5	11-06 06	7
21	27.79944	-97.40056	97.4	11-17 05	6	90.9	10-07 04	8
23	27.80028	-97.41528	181.8	10-17 05	21	130.7	10-06 00	17
25	27.75139	-97.4275	52.1	11-06 05	4	22.2	10-17 06	0
32	27.79472	-97.39639	40.4	11-17 05	5	65.9	10-06 00	6
34	27.75333	-97.42889	53.1	11-06 05	4	22.9	10-17 06	0
36	27.79056	-97.43028	179.8	11-17 06	15	122.3	11-06 06	28
38	27.7925	-97.40444	113.7	10-17 05	4	91.7	10-06 00	13
40	27.74222	-97.41444	41.5	11-06 05	1	18.6	10-17 06	0
43	27.78056	-97.40278	83.9	10-17 05	2	42.3	10-17 05	4
49	27.80056	-97.40278	112.2	11-17 05	6	105.7	10-07 04	9
51	27.79417	-97.68139	31.1	11-18 02	1	4.1	10-22 00	0
52	27.75667	-97.4525	35.1	11-17 06	2	26.2	11-18 05	0
56	27.79639	-97.66833	32.9	11-18 02	1	4.5	10-22 00	0
58	27.76694	-97.39722	33.2	10-17 05	1	25.0	10-17 06	0
59	27.78444	-97.41361	56.9	10-17 05	6	64.0	10-17 05	7
60	27.73361	-97.41667	46.4	11-06 05	1	15.2	10-17 06	0
62	27.72583	-97.44528	32.6	11-17 06	1	16.5	11-18 05	0
64	27.77472	-97.42667	93.6	11-06 05	6	42.3	11-18 04	3
65	27.795	-97.42222	129.8	11-06 05	24	143.7	10-17 06	23
66	27.75611	-97.43972	54.4	11-17 06	2	26.7	11-18 05	0
68	27.74389	-97.43361	50.1	11-17 06	3	19.2	10-17 06	0
70	27.79778	-97.43167	128.5	11-18 07	34	172.3	10-16 22	49
72	27.74833	-97.42917	46.9	11-06 05	4	21.1	10-17 06	0
75	27.79778	-97.42472	186.9	11-06 05	44	177.1	10-17 06	35
80	27.80528	-97.44694	169.1	11-18 02	56	205.3	10-22 00	50
82	27.77028	-97.42972	89.3	11-17 06	6	41.1	11-18 04	3
83	27.75639	-97.44361	47.9	11-17 06	1	27.9	11-18 05	0
84	27.7325	-97.41444	40.0	11-06 05	1	14.8	10-17 06	0
85	27.79167	-97.41222	134.9	10-17 05	6	105.5	10-17 05	15
87	27.83194	-97.55583	58.9	11-18 02	12	34.3	10-04 05	2
88	27.81944	-97.52389	158.4	11-06 05	25	113.3	11-18 07	26
92	27.86028	-97.62944	34.7	11-18 01	1	9.1	10-17 02	0
95	27.77083	-97.40278	33.8	10-17 05	1	30.2	10-17 06	1
96	27.79556	-97.66306	32.7	11-18 02	1	5.0	10-17 00	0
98	27.82745	-97.55122	51.5	11-01 02	10	38.9	10-21 23	8
112	27.79332	-97.40323	86.5	10-17 05	3	93.6	10-06 00	12
113	27.76394	-97.38195	50.7	10-17 05	1	21.1	10-06 01	0
114	27.76505	-97.42416	101.1	11-06 05	5	28.8	10-17 06	0
116	27.76165	-97.41269	37.7	11-18 05	2	25.9	10-17 06	0
117	27.78644	-97.39731	76.5	10-17 05	2	62.8	10-06 00	5

	Hospitals		AERMOD			CALPUFF		
receptor #	Lat	Long	Max. Conc. (PPBC)	Date of Occurrence mm-dd-hh	# of hours over 30 ppbC	Max. Conc. (PPBC)	Date of Occurrence mm-dd-hh	# of hours over 30 ppbC
121	27.77472	-97.40361	43.2	10-17 05	2	34.8	10-17 05	2
122	27.77583	-97.39417	71.6	10-17 05	2	32.9	10-06 01	1
124	27.77603	-97.39444	73.4	10-17 05	2	33.1	10-06 01	2
126	27.7797	-97.416	65.1	11-18 05	6	51.0	10-17 06	4
127	27.77795	-97.39633	78.2	10-17 05	2	35.7	10-06 01	4
129	27.77983	-97.41353	48.9	11-18 04	5	48.6	10-17 06	3

	University		AERMOD			CALPUFF		
receptor #	Lat	Long	Max. Conc. (PPBC)	Date of Occurrence mm-dd-hh	# of hours over 30 ppbC	Max. Conc. (PPBC)	Date of Occurrence mm-dd-hh	# of hours over 30 ppbC
138	27.80778	-97.46944	144.5	11-18 02	21	63.2	10-06 00	16
139	27.7625	-97.3925	30.9	10-17 05	1	21.4	10-17 06	0

* Receptor numbers are arbitrary given numbers for convenience

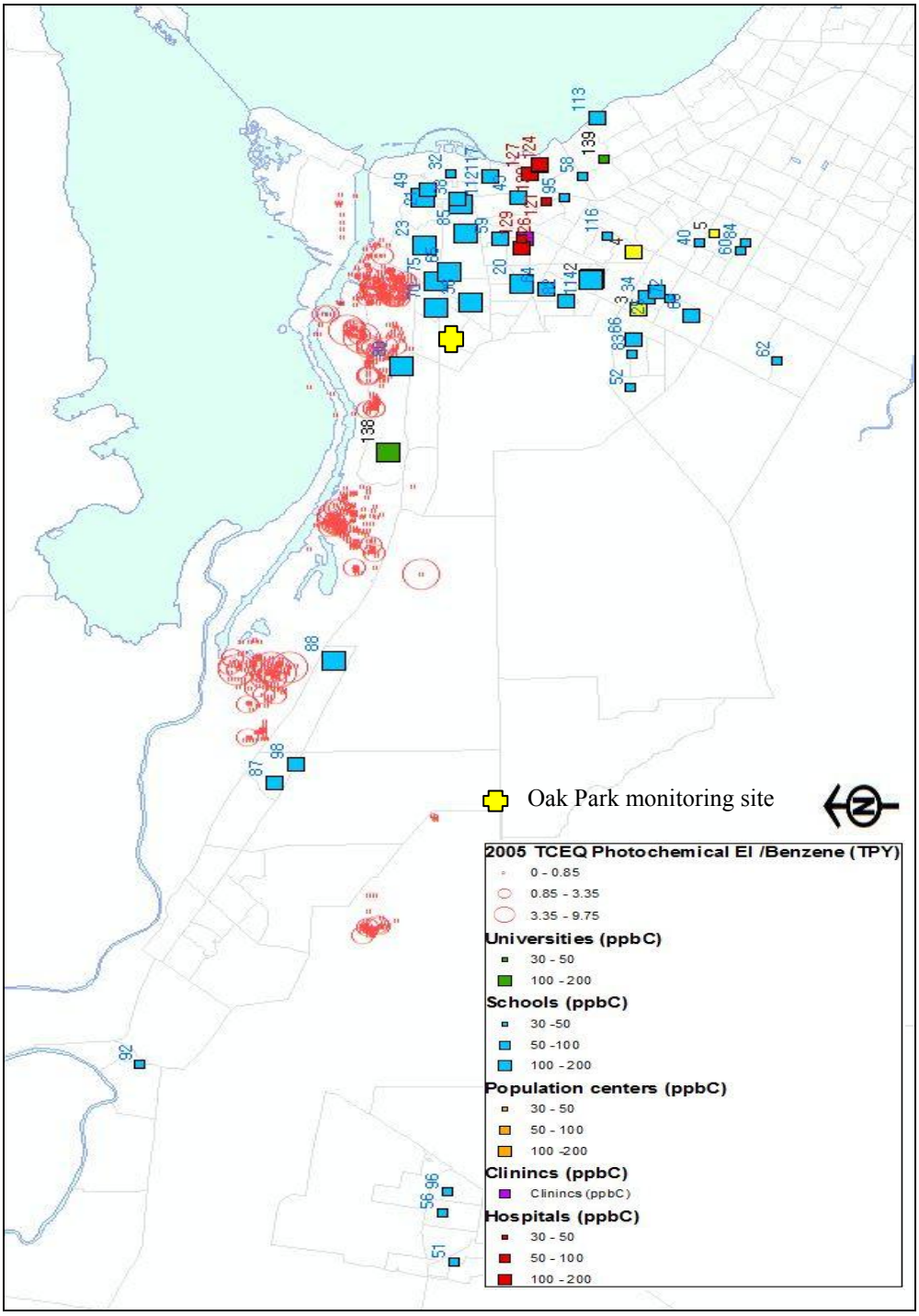

Figure 5.18 Discrete locations with predicted high benzene concentration (over 30 ppbC) with AERMOD (scaled with 1-hour maximum benzene concentration: ppbC)
* Benzene emissions from 2005 TCEQ Photochemical Modeling Inventory

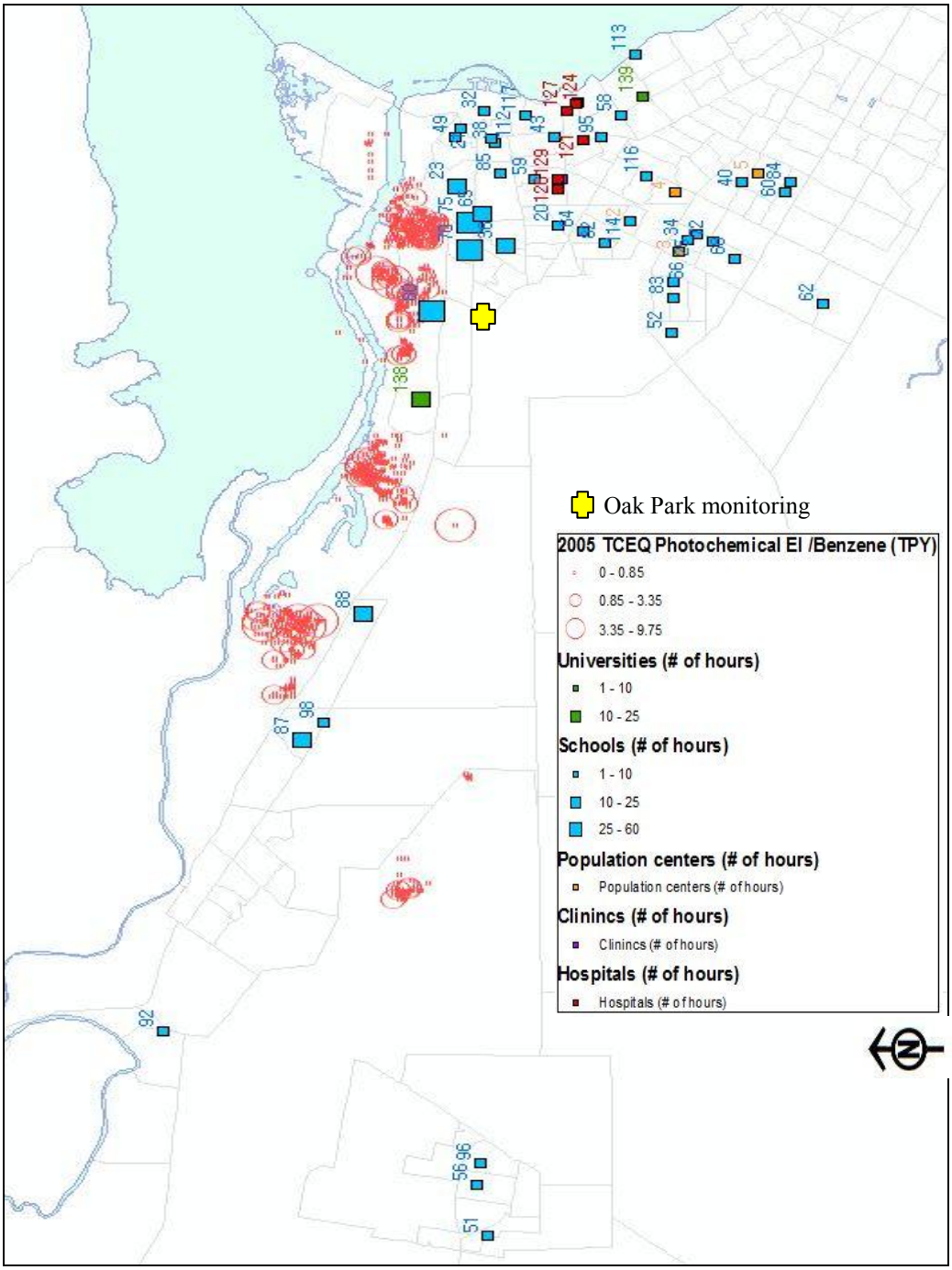

Figure 5.19 Discrete locations with predicted high benzene concentration (over 30 ppbC) with AERMOD (scaled with number of hours for 1-hour maximum benzene concentration)

* Benzene emissions from 2005 TCEQ Photochemical Modeling Inventory

More data on the date and time of day of predicted high benzene concentrations, during the Oct. – Nov. 2006, at the discrete receptors are summarized in Table 5.2 and Table 5.3. For the discrete receptors, AERMOD predicted 5 days with high benzene concentrations at 54 receptors, and CALPUF predicted 9 days for 30 receptors. Maximum benzene concentrations were likely to be predicted during night times till early morning hours (2200 CST to 0700 CST), which is consistent with results presented in Chapter 4 (Figure 4.16).

Table 5.2 Maximum benzene concentration predicted date and number of sites predicted at that date for AERMOD and CALPUFF including maximum benzene predicted time of day and the number of sites predicted at that time of day during the Oct. – Nov. 2006 period

AERMOD	
Predicted Date	# of sites
10-17	15
11-01	1
11-06	15
11-17	11
11-18	12

Predicted hour	# of sites
1:00 AM	1
2:00 AM	7
4:00 AM	2
5:00 AM	35
6:00 AM	8
7:00 AM	1

CALPUFF	
Predicted Date	# of sites
10-04	1
10-06	9
10-07	2
10-16	1
10-17	10
10-21	1
10-22	1
11-06	2
11-18	3

Predicted hour	# of sites
12:00 AM	7
1:00 AM	3
4:00 AM	4
5:00 AM	5
6:00 AM	8
7:00 AM	1
10:00 PM	1
11:00 PM	1

Table 5.3 compares the results of the Oak Park modeling with the modeling of the other receptor sites. The Table reports the date of predicted 1-hour daily maximum benzene concentration over 30 ppbC for 1) observations at the Oak Park monitoring site, 2) predictions by AERMOD and CALPUFF at the Oak Park location, and for 3) the other receptors. . The Oak Park site observed a total of 20 days during the 2 month period with high benzene concentrations (McGaughey et al. 2009). AERMOD predicted high benzene concentrations for 20 days, and CALPUFF predicted 19 days. . For the discrete receptors, 5 days of high benzene concentrations were predicted; for CALPUFF 9 days were predicted.

Table 5.3 Date of high benzene concentration (over 30 ppbC) for observation at Oak Park and AERMOD /CALPUFF predicted date for Oak Park and other discrete receptors during Oct. – Nov. 2006 period

Date of high benzene concentration	10-04	10-05	10-06	10-07	10-08	10-09	10-11	10-13	10-14	10-16	10-17	10-19	10-20	10-21	10-22	10-23	10-24
Observation at Oak Park																	
AERMOD at Oak Park																	
CALPUFF at Oak Park																	
AERMOD at discrete receptors																	
CALPUFF at discrete receptors																	

Date of high benzene concentration	11-01	11-02	11-03	11-04	11-05	11-06	11-07	11-11	11-12	11-13	11-16	11-17	11-18	11-19	11-20	11-21
Observation at Oak Park																
AERMOD at Oak Park																
CALPUFF at Oak Park																
AERMOD at discrete receptors																
CALPUFF at discrete receptors																

6 CONCLUSIONS AND RECOMMENDATIONS

Summary

Since 2005, The University of Texas at Austin (UT) has operated a dense ambient monitoring network that includes both hourly automated gas chromatographs as well as threshold triggered canister samples and meteorological data in the Corpus Christi area. The seven site network, incorporating both the industrial and residential areas in Corpus Christi, provided a unique opportunity to further the understanding of air quality modeling at a neighborhood scale. Two air dispersion models, AERMOD and CALPUFF, were used to predict air concentrations of benzene for one of the UT operated monitoring site (Oak Park monitoring site: C634) and was compared to the observed benzene concentration data at the Oak Park monitoring site to evaluate the model performance. AERMOD and CALPUFF were also used to predict benzene concentration in populated areas and at sensitive receptor locations such as schools and hospitals.

Observation data for benzene concentration at the Oak Park exhibits maximum daily concentrations mostly in early morning hours. High benzene concentrations (McGaughey et al. 2009) were likely observed within northern wind directions due to the location of the industrial facilities and Oak Park monitoring site. Both AERMOD and CALPUFF were able to reproduce the early morning high benzene concentration and the northern wind effect except for the NNE strong wind condition, where the observed data indicated elevated high benzene concentration which AERMOD and CALPUFF failed to. Moreover, the Oak Park site also observed high benzene concentration during 0800 CST to 1100 CST whereas the two dispersion models didn't predict. This could be an evidence of non-industrial emission sources such as mobile source emissions, since a major

roadway Interstate-37 crosses north to the Oak Park monitoring site. With the threshold of 30 ppbC high benzene concentration, the best predicted daily maximum concentration date was Oct. 6th for AERMOD and Oct. 21st for CALPUFF, but for the major three daily maximum concentration observed, both AERMOD and CALPUFF performed low. Especially for the highest daily maximum benzene concentration observed on Nov. 3rd, neither AERMOD nor CALPUFF could predict its concentration. It could be due to the NNE strong wind condition at that time of occurrence or attributed by different types of emissions other than the point sources emissions from the 2005 TCEQ Photochemical Modeling inventory, such as mobile source or accidental event. 24-hour Mean Normalized Gross Error average for the AERMOD and CALPUFF performed to be 120% and 107%, which is higher than the preferred range (35%) by Tesche et al. (1991). The Mean Normalized Bias for AERMOD exhibits changes within approximately two-week period, whereas CALPUFF shows a stronger negative bias relative to observed values.

One of AERMOD's significant limitations is its inability to incorporate meteorological data from more than one surface site. Sensitivity runs using different surface meteorology observed at other CCNAT monitoring sites (within the range of 10 km from the Oak Park site) was held for AERMOD. The Oak Park meteorological data produced higher benzene concentrations at the Oak Park location when compared to the prediction using other meteorological data collected (Solar Estates site, Port Grain site, and the J.I. Hailey site). These other meteorological data resulted with negative bias compared to the observation data and neither could predict the three major daily maximum benzene concentration observed. The low performance at the date of Nov. 3rd was in depth looked into for spatial dislocation possibility of the Oak Park site location within the two dispersion models. Unfortunately no evidence for the nearby Oak Park

locations predicting high benzene concentration was found. Terrain height dislocation possibilities and the option for stack-tip-downwash effect were also looked into for the Oak Park site with AERMOD but found no relations to the poor performance of un-matching high observed concentration data. Possible issue for this performance difference may be due to the lack of other emission sources such as mobile sources from nearby roadways. Propane was also used in AERMOD prediction at the Oak Park site location to verify the AERMOD model performance. Similar results with consistent daily maximum concentration occurrence date, and similar tendency of MNGE and MNB values compared to benzene's study shows the current performance limitation of AERMOD. A new version of AERMOD (ver. 09292) was released during this study. To ensure that the new version will not affect the overall results to this study, benzene prediction using the new version of AERMOD was performed. Though few modifications were included in the new version, the overall results were consistent. Sensitive receptor locations such as schools, hospitals, universities, clinics, and population centers were studied by AERMOD and CALPUFF to predict benzene concentration at these locations to verify potential health risk due to benzene exposure. Out of 54 sites, from the modeled 141 sensitive receptors in Corpus Christi area, predicted high benzene concentration (over 30 ppbC) during the Oct. – Nov. 2006 period by AERMOD, and 30 sites was predicted by CALPUFF. Maximum daily benzene concentrations for these sites mostly occurred during early morning hours by AERMOD, but CALPUFF predicted some maximum concentration to occur during late night (2200 CST to 0100 CST). With assumptions that when high benzene concentrations are detected at the Oak Park monitoring station, there are possibility of high benzene concentrations to occur on sensitive receptors, as most of the receptors are south to the Oak Park monitoring site which is in contiguity with the industries, AERMOD predicted

three dates out of five to have meaningful prediction over 30 ppbC, and CALPUFF matched six dates out of nine during the two month modeling period at the sensitive receptors.

Recommendations

Gaussian dispersion models are sensitive to emissions and meteorology inputs, and also spatial allocation (Sax et al. 2003). The two different dispersion model AERMOD and CALPUFF somewhat performed similarly during the Oct. – Nov. 2006 period for the Oak Park monitoring station at Corpus Christi. The dates which AERMOD couldn't predict, CALPUFF couldn't predict either. Uncertainties for meteorology exists in AERMOD since it incorporates only a single set of meteorological data, whereas CALPUFF potentially overcome this issue by CALPUFF using three-dimensional wind and temperature fields that incorporate meteorological data from multiple sites. Low performance of AERMOD and CALPUFF for strong NNE winds can also be an issue for the models performance due to building downwash algorithms to be looked into. One of CALPUFF's option not used in this study is slugs, considered as a group of overlapping circular puffs with small separations, which can be important in near-field approach (Turner et al. 2007, CALPUFF Users Guide 2000). AERMOD have recently released a new version (ver. 09292) with modified options for terrain and deposition calculations (http://www.epa.gov/ttn/scram/models/aermod/aermod_mcb3.txt) which could be considered in comparison. Conducting longer period modeling and inter-comparison with the observed data from other CCNAT monitoring sites would be useful to further assess the model performance. Most of all, there are others sources of air toxic emissions beside industrial facilities, such as mobile sources and small stationary sources, which were not included in this modeling but should be considered for the next phase study. Though the

predicted values for 1-hr benzene concentrations for sensitive receptor locations were below the TCEQ's 1-hr Effects Screening Levels (ESLs), 324 ppbC, we should note that this study did not include the mobile emissions and other stationary sources which are possibly located nearby the sensitive receptors. Furthermore, as predicted maximum concentration values were likely to occur during night times and early hour mornings, different benzene exposure rate should be considered for places where people stay during the daytime (e.g. schools, clinics, universities, etc) and evening-night time hours (e.g. residential area).

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